Reactivity of $(THF)_4Ca(PPh_2)_2$ in Stoichiometric and Catalytic Reactions

Dissertation

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von Master-Chem. Tareq Al-Shboul
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1. Gutachter:	Prof. Dr. Matthias Westerhausen, FSU Jena
2. Gutachter:	Prof. Dr. Rainer Beckert, FSU Jena
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DEDICATIONS

To

Candles of my life, Father and Mother

My Wife

My Brothers and Sisters

All my Family, Friends

With Love

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List of Abbreviations

Å…….....	Angstrom
δ…….....	Chemical shift
z…….	Charge
J……..	Coupling constant (NMR)
d…….	Doublet (^{1}H NMR)
dd……...	Doublet of doublets (^{1}H NMR)
ddd……	Doublet of doublets of doublets (^{1}H NMR)
Hz……...	Herz
hmpa……...	Hexamethylphosphoramide
IR……	Infrared
i……...	Ipso
L…….....	Ligand
M…….....	Metal
Mes……	Mesityl
Me…….	Methyl
m……	Multiplet (1H NMR)
MS……..	Mass spectrometry
m……	Meta
m……	Medium (IR)
NMR……...	Nuclear magnetic resonance
o……..	Ortho
p……..	Para
PDI …….....	Polydispercity
PCL…….....	Poly(ε-caprolactone)
PGA…….....	Poly(glycolic acid)
PLA…….....	Poly(L-lactic acid)
ROP…….....	Ring opening polymerization
r.t……...	Room temperature
s…….	Singlet (^{1}H NMR)
s…….	Strong (IR)

^{t}Bu…….....	Tertiary Butyl
tmhd…….....	2,2,6,6-Tetrametylheptane-3,5-dione
TOF …….....	Turnover frequency
THF…….....	Tetrahydrofuran
TMEDA…….....	Tetramethylethylenediamine
w……	Weak (IR)
w%.....	Weight percent

1. Introduction

1.1. General

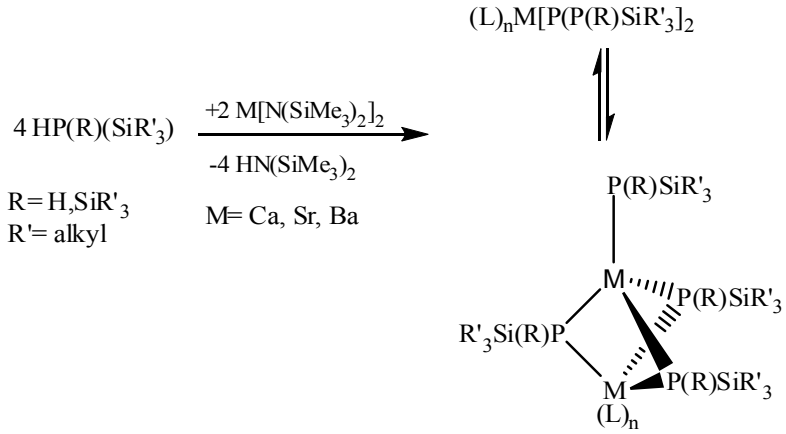
Until the mid-1980s, the organic derivatives of calcium, strontium and barium possessed the dual status of being among the longest known yet least understood of any class of organometallic complexes. Few years after the discovery of Grignard reagents in 1900, the first reports of analogous compounds of the heavier alkaline-earth metals began to appear. The development of an organometallic chemistry of the heavy alkaline earth metals calcium, strontium and barium has increased enormously during the last two decades. During the first part of this period, metallocenes and other cyclopentadienyl-containing compounds dominated the organometallic chemistry of these elements.

Calcium is the fifth most abundant element in earth's crust but does not occur naturally in the free state. In addition, it is one of the most widespread metals on earth and one of the very few metals with no toxicity regardless of the concentration [1]. Calcium also plays an extremely important role in advanced biological systems; sophisticated control mechanisms regulate the concentration of these metal ions in metabolic systems [2]. Moreover, the earth's crust including atmosphere and hydrosphere contains 3.4 % by weight of calcium [3]. It is found in nature as carbonate, sulphate, silicate, phosphate, and fluoride. In all these compounds calcium is considered as redox-inert and always exhibited the oxidation state of +2. Calcium is also essential for living organisms and the most abundant element in the human body. The average adult contains over 1 kg of calcium, stored mainly as calcium salts in the bones. Calcium is essential for the normal activity of muscles and nerves, for growth of bones and teeth, and for blood clotting.

The heavy alkaline earth metals possess intermediate positions between the alkali metals and the elements of the scandium group. The cations of the alkali, alkaline earth and group III metals are isoelectronic and show no redox activity. However, the rather large electronegativity difference of the alkali metals (which represent characteristic s-block metals) and carbon lead to highly ionic compounds which are salt-like and low-soluble in common organic solvents [4]. Due to this consideration, the investigations on the organometallic chemistry of alkaline earth metals remained superficial to the metallocene chemistry for many decades. The determination of the structure of polymeric calcocene by Stucky and Zerger [5] led to vast development of the metallocene chemistry of the heavy alkaline earth metal which was summarized in several articles [6].

1.2. Phosphanides of Calcium

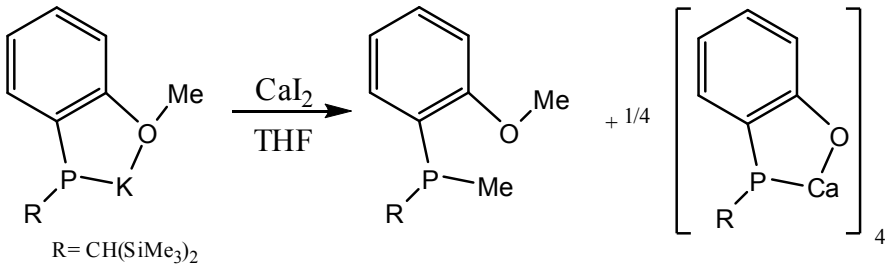
Phosphanides of the calcium, as well as those of strontium and barium, found the interest of several research groups [7]. The magnesiation of phenylphosphane with dibutylmagnesium gave polymeric $Mg[P(H)Ph]_2$ which was transferred into monomeric (tmeda)-$Mg[(H)Ph]_2$ (Mg-P 258.7(5) and 259.2(5) pm) by addition of 1,2-bis(dimethylamino)ethane [8]. Magnesium bis(diphenylphosphanide) was prepared either *via* metallation of $HPPh_2$ with MgR_2 (R = Et, Ph) or *via* the metathesis reaction of $MgBr_2$ with $KPPh_2$ in THF [9]. In order to ensure solubility in common organic solvents one or two trialkylsilyl substituted phosphanides of the heavier alkaline earth metals were prepared according to equation (1) [10].



(1)

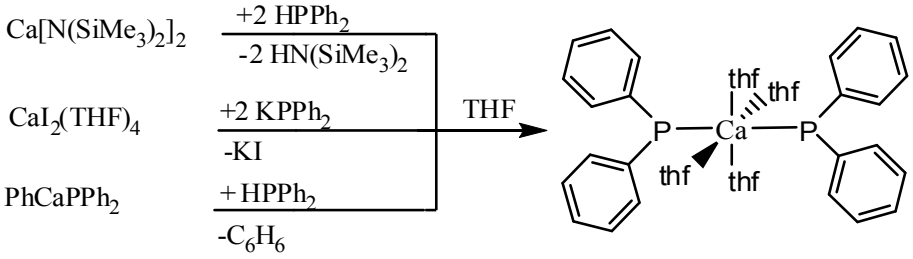
In contrast to the bis(trimethylsilyl) amides, which are accessible *via* a transmetallation of $Sn[N(SiMe_3)]_2$ [11], the reaction of $[Sn\{P(SiMe_3)_2\}_2]_2$ with calcium yielded heterobimetallic cages containing calcium, tin(II) and phosphorous [12,13]. Magnesium underwent metal-metal exchange reaction with $[Sn\{P(SiMe_3)_2\}_2]_2$ without formation of heterometallic cages [14]. Alkaline earth metal bis(phosphanides) were synthesized in good yields by metallation of $HP(SiR_3)R'$ (R'= H, SiR_3) with the alkaline earth metal bis[bis(trimethylsilyl)amides] [10]. In contrast to the large difference of trialkylsilyl substituted phosphanides of the alkaline earth metals [10], there are only few reports on alkyl and aryl-substituted phosphanides. The reaction of Ph_3C-$Ca(THF)_2Cl$ with diphenylphosphane yielded heteroleptic Ph_2P-CaCl [15]. The bidentate phosphane complex $(THF)_3Ca[(Me_2P)_2C\text{-}SiMe_3]_2$ with seven coordinate calcium atoms was prepared *via* a metathesis reaction of $CaCl_2$ with the corresponding lithium compound and the Ca-P bond lengths were found in the range of 303.8(1) - 304.9(1) pm [16]. The reaction of CaI_2 with $K[P\{CH(SiMe_3)_2\}C_6H_4\text{-}2\text{-}OMe]$ gave the calcium tetramer which was accompanied by

cleavage reactions yielding phosphanes shown in equation (2) [17]. In this calcium complex, the Ca-P distances of 296.12(6) and 296.95(7) pm were observed.



(2)

The strontium and barium phosphanide complexes were prepared by metallation of $HPPh_2$ with the metals in THF. However, the reaction of calcium metal with $HPPh_2$ does not proceed [18]. Suitable pathways for the preparation of the corresponding Ca-phosphanide include the metallation of $HPPh_2$ with $Ca[N(SiMe_3)_2]_2$ [19], the metathesis reaction of $CaI_2(THF)_4$ with two equivalents of $KPPh_2$ [18] or the metallation of $HPPh_2$ with $[(THF)_4Ca(Ph)(Ph_2)_2]$ according to equation (3).



(3)

The molecular structure of the Ca-phosphanide, shown in Figure 1.1, represents a *trans* arrangement of the phosphanide substituents with Ca-P bond lengths of 298.65(6) [18] and 298.82(4) pm [19]. Reduced steric strain led to aggregation and oligomerization and formation of $Ca[P(H)Ph_2]_2$ with bridging phenylphosphanide substituents [20].

Figure 1.1: Molecular structure of $(thf)_4Ca(PPh_2)_2$. Hydrogen atoms are neglected for clarity reasons (adapted from Reference [130d]).

1.3. Calcium-mediated Catalysis:

1.3.1. Calcium-mediated polymerization reactions:

It is highly preferable to use nontoxic catalysts in the synthesis of biopolymers intended for biomedical and pharmaceutical applications, since complete removal of catalyst from the polymer is often impossible. Calcium-based catalysts may serve this purpose.

The non-toxicity of calcium regardless of the concentration initiated tremendous efforts in preparation of calcium-based catalysts for the synthesis of biopolymers. Biopolymers have to fulfil certain requirements for the use as artificial tissues and as materials for surgical sutures. The demand for these materials is extremely high with respect to toxicity and immunogenic, allergic reactions. Furthermore, the polymeric materials should give no toxic degradation products and have suitable mechanical properties [21]. Theses tissues often are polyesters, polyanhydrides or polyamides. Due to the fact that the anionic polymerization initiator remains in the polymeric materials, organometallic compounds based on calcium are the ideal starting materials for ring-opening polymerization.

A convenient method for the synthesis of polyesters is the ring-opening polymerization (ROP) of cyclic esters (Figure 1.2). Due to the advantages of well controlled molecular weight and low polydispercity (PDI) of polymers, many chemists focused on the

development of new catalysts for ring opening polymerization. Consequently, some review articles on polymerization of lactide have been published [22-24]. Few examples of discrete calcium complexes have been reported in the polymerization of lactides and cyclic esters especially by Chisholm and Feijen groups.

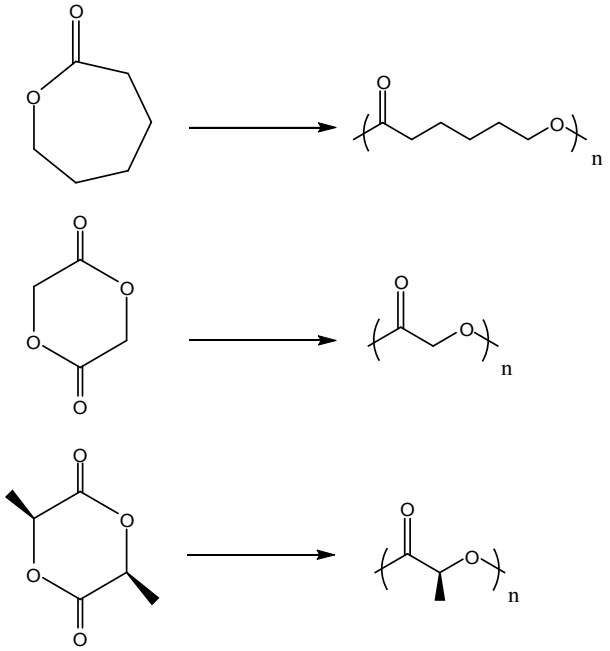
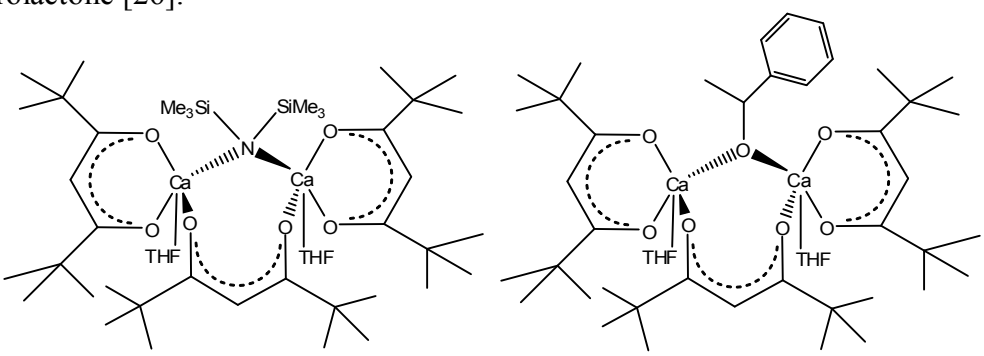


Figure 1.2: Ring-opening polymerization of selected cyclic lactones to give the following: a) poly(ε-caprolactone) (PCL); (b) poly(glycolic acid) (PGA); poly(L-lactic acid) (PLA).

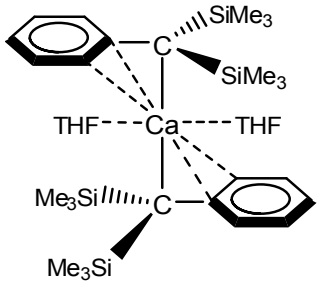
Calcium isopropyloxide generated *in situ* from the reaction of bis(tetrahydrofuran) calcium bis[bis(trimethylsilyl)amide] and isopropanol, is highly active for the living and controlled ring-opening polymerization of cyclic esters in THF using mild condition (18 ºC) [25]. Promoted by this fact, Feijen *et al.* synthesized two single-site calcium initiators containing sterically hindering tmhd ligands (H-tmhd = 2,2,6,6-tetrametylheptane-3,5-dione) $[(THF)Ca(tmhd)]_2[\mu\text{-}N(SiMe_3)_2](\mu\text{-tmhd})$ (**1**) and $[(THF)Ca(tmhd)]_2[\mu\text{-OCH(Me)Ph}](\mu\text{-tmhd})$ (**2**) (Figure 1.3) and applied them for the ring-opening polymerization of L-lactide and ε-caprolactone [26].



1 **2**

Figure 1.3: Diketone supported calcium complexes **1** and **2**.

Single-site initiators are of interest since the bulky chelating ligand might suppress side reactions (e.g. inter- and intra-transesterifications [27]) and some of these initiators could even bring about a stereoselective polymerization of lactides [28]. The tmhd ligand was chosen because it is simple and capable of imparting stability and solubility to many metal complexes. Feil and Harder published the structures of the first homoleptic dibenzylcalcium complexes **3** [29]**, 4** [30] and heteroleptic dibenzylcalcium complex **5** [31]. These complexes initiate the anionic living polymerization of styrene.



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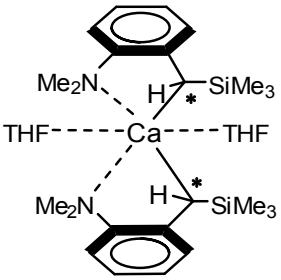

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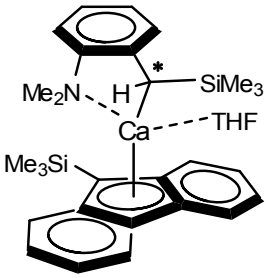

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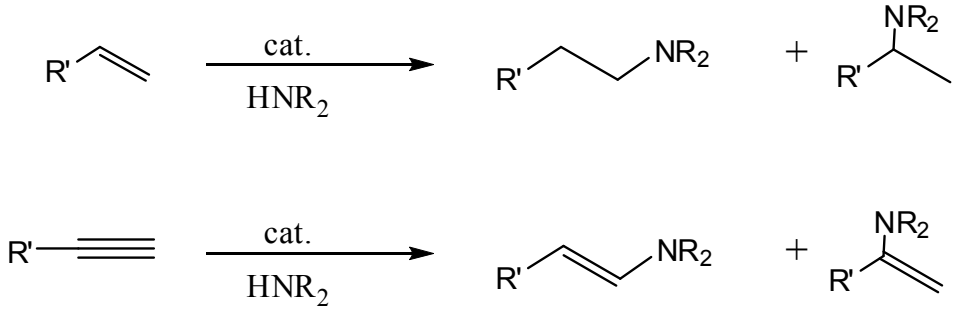
The heteroleptic benzylcalcium compound **5** is isolobal to $CpTiMe^{+}$, a species proposed to be active in the highly syndiotactic polymerization of styrene [32].

1.3.2. Calcium-mediated hydroamination reactions:

The catalytic addition of an organic amine N-H bond to carbon-carbon multiple bonds (hydroamination) to give nitrogen-containing molecules is of great interest to both academic and industrial researchers alike according to equation 4 [33, 37].



(4)

At the present time most amines are made in multistep syntheses, and as such, hydroamination offers an attractive alternative to give nitrogen-containing molecules that are important for fine chemicals and pharmaceuticals and as useful chiral building blocks. It has been shown that hydroamination can be catalyzed by d- [34-36] and f-block [37, 38-46, 56] transition metals, alkali metals, [47] and more recently by copper, [48] silver, [49] gold, [50]

and zinc [51, 57]. On the one hand, early transition metals and the lanthanides are highly efficient catalysts for the hydroamination reaction of various C-C multiple bonds, but the high sensitivity of these catalysts toward moisture and air limits their synthetic application. Furthermore, they show a very limited tolerance to polar functional groups. On the other hand, late transition metal catalysts offer an advantage of greater polar functional group compatibility. However, most of these catalysts are based on the relatively expensive platinum metals [35] or on nickel [33, 35] which has only a limited use for the synthesis of pharmaceuticals. Moreover for nonactivated substrates most of the late transition metal catalysts show limited scope and modest selectivity. Therefore, there is a demand for new catalysts for the hydroamination. In this context Hill *et al.* [52] reported that the *β*-diketiminate-stabilized calcium amide [{HC(C(Me)$_2$N-2,6-*i*Pr$_2$C$_6$H$_3$)$_2$}Ca{N(SiMe$_3$)$_2$}(THF)] (Figure 1.4), a compound originally reported by Chisholm and co-worker as a catalyst for the polymerization of *rac*-lactide [53], is a highly effective catalyst for the intramolcular hydroamination of aminoalkenes and aminoalkynes. The low cost and availability of calcium offer significant commercial advantages.

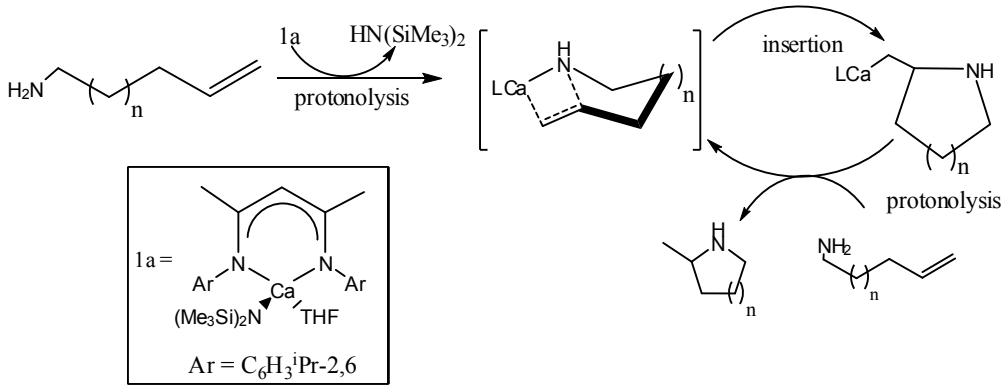
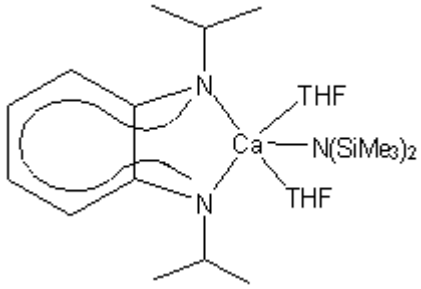


Figure 1.4: Generalized postulated catalytic cycle for calcium-mediated intermolecular hydroamination.

The reaction was postulated to occur by the generalized catalytic cycle outlined in Figure 1.4, which was assumed, by direct analogy to the experimentally validated cycle in lanthanide-mediated hydroamination reactions, to proceed *via* both σ-bond metathesis (protonolysis) and intermolecular C=C insertion for catalyst activation, thereby continuing the catalytic turnover. On the basis of these results Roesky *et al.* [54] recently reported on the calcium amido complexes [(*i*PrAT)Ca{N(SiMe$_3$)$_2$}-(THF)]$_2$ (*i*PrAT=2-(isopropylamino)troponate) and [{(*i*Pr)$_2$-ATI}Ca{N(SiMe$_3$)$_2$}(THF)$_2$] ((*i*Pr)$_2$ATI=*N*-isopropyl-2-(isopropylamino)troponiminate) **6**, which showed for some substrates a similar activity to the

β-diketiminato system as catalysts for intramolecular hydroamination [55]. They used the ligands 2-(isopropylamino)tropone, (*i*PrAT)H, and *N*-isopropyl-2-(isopropylamino) troponimine, {(*i*Pr)$_2$ATI}H, which have been successfully employed in rare earth [56] and zinc chemistry [57]. Their complexes have proven to be highly active catalysts for the intramolecular hydroamination/cyclization reaction. It was shown earlier that the reaction of [{(*i*Pr)$_2$ATI}-Li(THF)$_2$] with CaI_2 does result only in the complex [{(*i*Pr)$_2$ATI}Ca(THF)$_2$I$_2$Li$_2$(THF)$_2$] [58].



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1.3.3. Calcium-mediated hydrosilylation reactions:

The direct process and the hydrosilylation reaction are probably the two most important reactions in organosilicon chemistry in that they are able to produce Si-C bonds [59]. In its most widely used form, hydrosilylation is the reaction where hydrosilanes Si-H add to unsaturated substrates [60, 61]. There are several methods to initiate this highly atom-efficient key transformation. Classical thermal and radical-initiated reactions often lead to oligomers, especially when readily polymerizable alkenes (e.g. styrenes) are used [62]. The conventional hydrosilylation of alkenes is catalyzed by [H_2PtCl_6]·6H_2O/*i*PrOH (called the Speier catalyst) [62]. The catalyst was replaced later by the more selective and reactive Karstedt (1,3-divinyl-1,1,3,3-tetramethyldisiloxane platinum complex) catalyst [63]. However, in some cases poor regiocontrol and side reactions, such as alkene isomerisation and hydrogenation, are still an issue [64]. The last decade has seen the development of lanthanide-based catalysts for this process [65, 72]. Although these catalysts show poor regioselectivity in some cases, they certainly feature several advantages, such as i) tunability of the regiochemistry by metal size and ligand choice and ii) enantioselective hydrosilylation. Hydrosilylation catalyzed by $LiAlH_4$ has been described but requires highly reactive SiH_4 and high pressure, which result in multiple hydrosilylation [66]. The only representative catalysts from the main-group elements are the Lewis acids $AlCl_3$ and $B(C_6F_5)_3$ [67] (Figure 1.5).

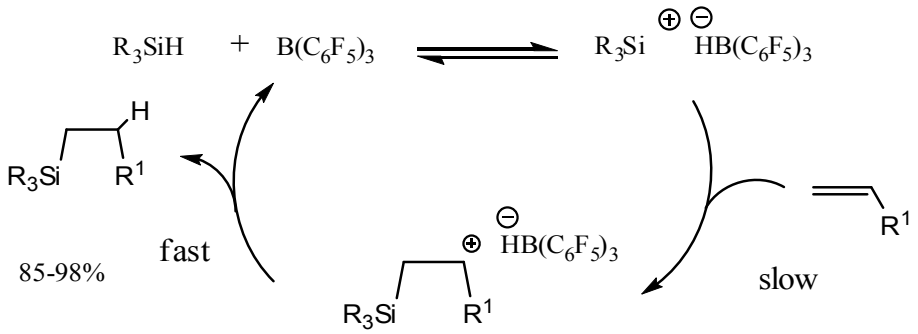


Figure 1.5: The highly efficient $B(C_6F_5)_3$-catalyzed hydrosilylation of alkenes following Rubin, Schwier and Gevorgyan [67].

The boron-catalyzed hydrosilylation reaction gives a new approach to the particularly difficult synthesis of silicon-sulfur bonds (Si-S) *via* the addition of Si-H to thioketones [68].

As organometallic complexes of the heavier alkaline earth metals show similarities with organolanthanides [69] and are increasingly used in catalysis [70-72], they could be potential candidates for early main-group metal hydrosilylation catalysts. Harder *et al.* suggested the catalytic hydrosilylation of alkenes with early main group metal catalysts [73] from which they proposed a mechanism similar to that for lanthanide catalysts [72] (Figure 1.6).

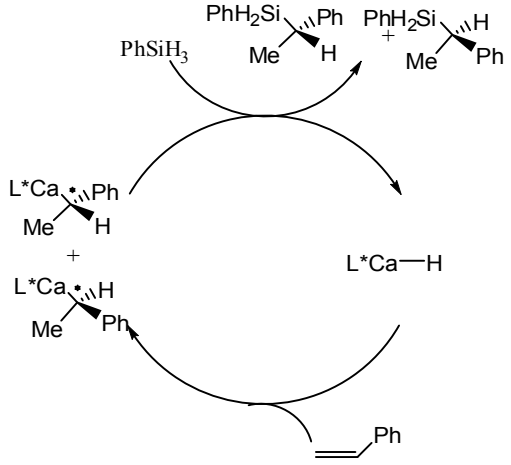
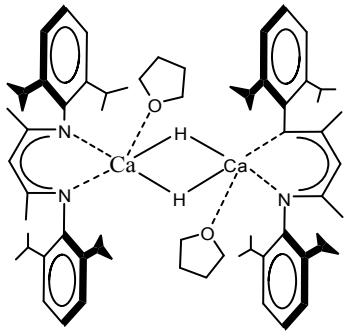


Figure 1.6: Catalytic cycle for hydrosilylation with lanthanide catalyst; L* represents the chiral ligands.

While these catalysts cannot compete with the well-established class of highly active transition metal catalysts [74, 62, 63], they display some remarkable features. Complete regiocontrol of the hydrosilylation reaction, which in some cases could be switched by either solvent or metal choice, was observed. Additionally, use of catalysts based on the much cheaper and biocompatible calcium could certainly be of interest for potential applications [74].

Since Ca-mediated hydrosilylation of alkenes is limited to activated alkenes, e. g. conjugated alkenes, styrene was chosen as an appropriate prochiral substrate. Hydrosilylation of styrene with phenylsilane using the benzylcalcium catalyst **2** [29] was shown to be fast and completely regioselective [73]. Use of calcium amide as catalyst requires the catalytic activity of the calcium amide functionality. Buch and Harder found that $[(Me_3Si)_2N]_2Ca(THF)_2$ is also an efficient, but somewhat less active catalyst for hydrosilylation reaction giving exclusively one regio-isomer [74]. Catalytic hydrosilylation of ketones, i.e. the formal addition of a silane R_3SiH to a ketone $R'_2C=O$ to give $R_3Si\text{-}OCHR'_2$, is a convenient one-step procedure for preparation of protected alcohols [75, 60, 61]. Several catalysts for this conversion are based on typical transition metals (Ni, Pd, Rh) but also catalysts based on Sn [76], Cu [77], Zn [78], Li and Na [79] have been reported. It has been shown that a strong Lewis acid like $(C_6F_5)_3B$ also efficiently catalyzes this reaction [80]. Spielmann and Harder reported that the calcium hydride complex **7** is an effective catalyst in the hydrosilylation of ketones [81].



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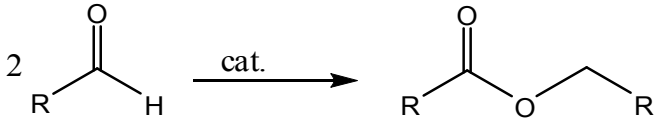
Independent from the silane/ketone ratio, a strong preference for the formation of bis-alkoxy silanes $[PhSiH(OR)_2]$ was observed.

1.3.4. The Tishchenko reaction:

The Tishchenko reaction (also known as Claisen–Tishchenko reaction), which has been known for about a century [82], is a useful method for the preparation of carboxylic acid esters from the dimerization of aldehydes (equation 5) [83]. This reaction is used industrially for the preparation of a wide range of monoesters which have been used as solvents, paint ingredients, lubricants, in addition to its applications in the food and perfume industries.



(5)

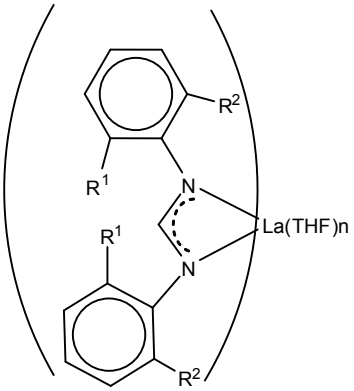
Recent homogeneous catalysts elaborated for Tishchenko reaction has made remarkable progress in activity in comparison with traditional aluminium alkoxides [82, 84, 85, 93-96b]. However, several important problems are still there in the advanced homogeneous catalysts for Tishchenko reaction. For instance, the separation of those homogeneous catalysts from the resulting solution causes loss of catalysts and reduces the product yields. Moreover, most of those homogeneous catalysts are toxic and expensive organometallic complexes.

In 1974, Tanabe and Saito found that MgO, CaO and BaO, which possess both acidic and basic sites, can catalyze the Tishchenko reaction of benzaldehyde *via* the formation of the active species of surface metal benzylate [86]. More recently, alumina-supported KF was also found to be successfully applicable to the Tishchenko reaction [87, 88]. Alkaline earth oxides and alumina-supported KF are classified as solid base catalysts or heterogeneous basic catalysts, and have been used in base-catalyzed reactions with infinite success [89, 90]. Solid base catalysts, unlike homogeneous catalysts, can be easily separated from the reaction mixture after carrying out the reaction, and are inexpensive and environmentally benign. These excellent properties emphasize the importance of the replacement of the homogeneous catalysts with the heterogeneous ones both in the laboratory and in the industrial processes utilizing Tishchenko esterification [91]. The alternative catalysts such as $K_2[Fe(CO)_4]$ [92], Cp_2MH_2 (M = Zr, Hf) [93], $B(OH)_3$ [94] and $[H_2Ru(PPh_3)_2]$ [95], also display moderate activities for the dimerization of benzaldehyde to benzyl benzoate. However, these alternative catalysts are either only reactive under extreme reaction conditions (e.g. boric acid) or they are slow (e.g. $[(Cp)_2ZrH_2]$) [93], or give low yields (e.g. $K_2[Fe(CO)_4]$) [92].

More recently, homoleptic lanthanoide amides, $M[N(SiMe_3)_2]_3$ (M = Sc, Y, La), have been reported as highly active catalysts for the Tishchenko reaction, mediating the dimerization of aromatic and aliphatic aldehydes to the carboxylic esters with turnover frequencies (TOF) ranging from 2 to 1500 h^{-1} [96]. In this case, the reaction mechanism has been investigated and suggested to occur *via* the formation of intermediate lanthanoide(III) alkoxides [96]. The advantages of these compounds as catalysts include the environmentally benign nature of the metals, their high activity, high stability, high Lewis acidity and easily interchangeable ligand spheres. Moreover, the homoleptic bis-(trimethylsilyl)amides of the alkaline earth metals $[M\{N(SiMe_3)_2\}_2]$ (M = Ca, Sr, Ba) were reported as pre-catalysts for the Tishchenko reaction, and were almost as active as the lanthanoide compounds [97].

Recently, a series of tris(formamidinato)lanthanum(III) complexes $[La(o\text{-TolForm})_3(thf)_2]$, $La(XylForm)_3(thf)]$ and $[La(EtForm)_3]$ (Figure 1.7) have been reported as pre-catalysts for the Tishchenko reaction [98]. These compounds are, for most of the conversions described,

more active than any other system reported. The tris(formamidinato)lanthanum(III) complexes were reported to be accessible from the reaction of *N*,*N*´´-bis-(aryl)formamidines (FormH) with lanthanoide metals and bis(pentafluorophenyl)mercury [$Hg(C_6F_5)_2$] in THF [99].



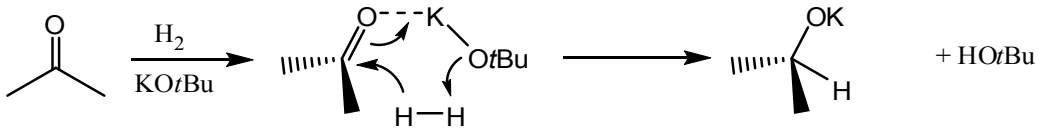
R^1 = Me, R^2 = H, n = 2
R^1 = R^2 = Me, n = 1
R^1 = R^2 = Et, n = 0

Figure 1.7: A series of tris(formamidinato)lanthanum(III) complexes [La(*o*-TolForm)$_3$(thf)$_2$], La(XylForm)$_3$(thf)] and [La(EtForm)$_3$].

1.3.5. Calcium-mediated hydrogenation reactions:

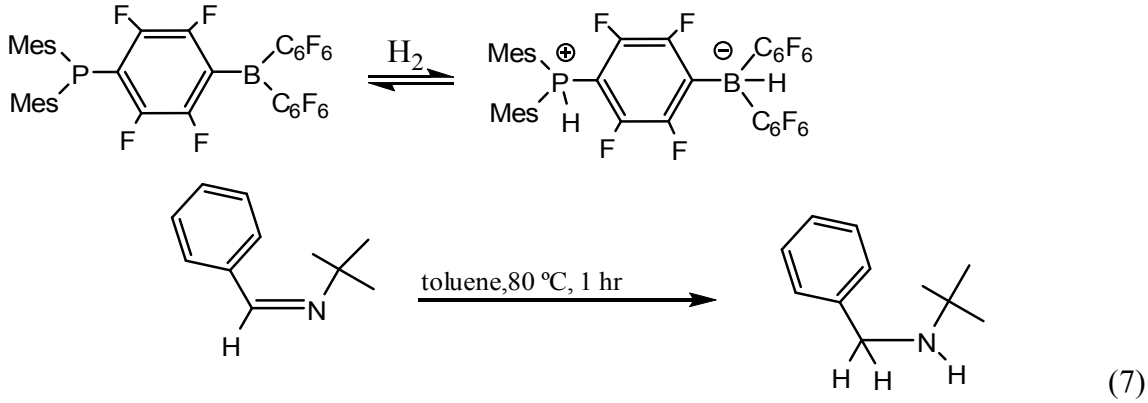
Hydrogenation is the chemical reaction that results from the addition of hydrogen (H_2) to unsaturated substrates. The process is usually employed to reduce or saturate organic compounds. Such reactions are used for the production of numerous chemicals worldwide, from large scale operations including the upgrading of crude oil and the production of bulk commodity materials to the synthesis of a variety of fine chemicals used in food, agricultural, and pharmaceutical industries [100]. This precursor is mediated by either homogeneous or heterogeneous transition-metal-based catalysts [100]. Blaser *et al.* [101] place the importance of this chemistry in context, stating that "hydrogen is the cleanest reducing agent and hydrogenation is arguably the most important catalytic method in synthetic organic chemistry both on the laboratory and the production scale". In 1897, Sabatier discovered that the introduction of a trace of nickel as a catalyst facilitated the addition of hydrogen to molecules of gaseous hydrocarbons in what is now known as the Sabatier process. For this work, Sabatier shared the 1912 Nobel Prize with Grignard. In the 1960s, the start of organometallic chemistry gave rise to homogeneous transition-metal-based hydrogenation catalysts for a variety of substrates. The operation of these catalysts hinges on the key step of oxidative

addition of hydrogen [102]. More recently, transition-metal systems that effect heterolytic cleavage of hydrogen at a metal center have been uncovered. In these cases, a metal hydride is formed with concurrent protonation of an amido ligand [103,104]. Non-transition-metal catalysts, such as KO*t*Bu, have been shown to act as a catalyst affecting the addition of H_2 to ketone under very high temperature (equation 6) [105].



(6)

Power *et al.* reported the hydrogenation of Ge_2-alkyne analogues to give a mixture of Ge_2 and primary germane products [106]. More recently, Bertrand *et al.* have confirmed that selected carbenes exhibit transition-metal-like reactivity and cleave hydrogen to effect a formal oxidative addition of the carbene C atom [107]. In recent work, small organic molecules have been shown to activate hydrogen [107,108] and the first metal-free catalysts for the addition of H_2 to ketone and imine have been introduced [108e, 109]. The latter organocatalytic reaction is based on heterolytic cleavage of H_2 by the unique reactivity of frustrated Lewis pairs (equation 7).



(7)

The reduction of nitrobenzene to aniline has been reported using fullerene, its mono-anion and hydrogen using UV radiation at atmospheric pressure [110]. Until now, few articles on the use of main-group metal catalysts in alkene hydrogenation have been published. Iodoboranes were introduced as Lewis acid catalysts for the liquefaction of coal by hydrogen (280–350 ºC, 150–250 bar H_2) [111a]. Earlier reports on hydridic hydrogenation catalysts including processes mediated by soluble $LiAlH_4$ [111b] or by suspensions of NaH, KH, and MgH_2 [111c] have been demonstrated. In all cases, reaction conditions are extreme (150–225

ºC, 60–100 bar H_2) and various products, including oligomers and polymers, were obtained. Recently, Harder *et al.* also reported that the calcium hydride **7** [81, 112] is an effective catalyst in the hydrogenation of conjugated alkenes [113]. A possible mechanism for the calcium-mediated hydrogenation of alkenes (Figure 1.8) is similar to that for organolanthanide-catalyzed alkene hydrogenation [114].

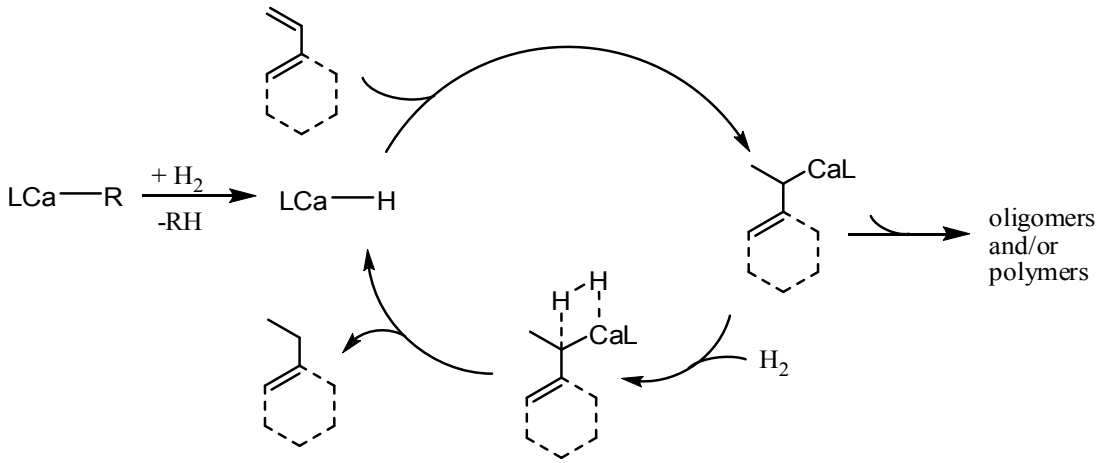


Figure 1.8: Proposed catalytic cycle for calcium-mediated hydrogenation of conjugated alkenes, L= ligand.

1.3.6. Calcium-mediated hydrophosphanylation:

Hydrophosphanylation is the addition of trivalent phosphine compounds to carbon-carbon multiple bonds. It is a simple method for the synthesis of organophosphorus compounds [115]. In contrast to the ready availability of hydrophosphanylation reactions in which pentavalent phosphorus compounds are involved, [116] hydrophosphanylation by metal catalysis often encounters difficulties.

Vinylphosphanes play an important role as ligands at catalytically active metal atoms. Some special examples are 1,4-bis(diphenylphosphanyl)buta-1,3-dienes (NUPHOS) which were prepared firstly by Doherty and coworkers [117,118] *via* a multi-step synthesis involving a coupling of alkynes at zirconium, a metal-metal exchange in order to obtain the copper derivative, followed by a quenching with $ClPPh_2$. Comparisons with other well-established ligands such as 2,2'-bis(diphenylphosphanyl)-1,1'-binaphthyl (BINAP) [119,120] and 2,2'-bis(diphenylphosphanyl)biphenyl (BIPHEP) [121,122] showed the advantages of these conformationally more flexible NUPHOS ligands. Thus far, 1,2,3,4-tetramethyl- and 1,2,3,4-tetraphenyl-NUPHOS were applied as ligands in catalytically active metal complexes. Diphenyl-vinylphosphanes can also be reductively coupled by lithium yielding 1,4-bis(diphenylphosphanyl)butanes [123].

Hydrophosphanylation can be performed successfully with many transition metal-based catalysts [116a, 124] and sometimes even metal-free [125]. Common metals in hydrophosphanylation reactions of alkynes or butadiynes are transition metals and lanthanoids such as cobalt, copper, lanthanum, nickel, palladium, rhodium, ruthenium, samarium, ytterbium, yttrium, zirconium, and others. Substitution of these – often expensive – noble transition metals by calcium would allow a more economic catalysis, even though lower turn-over numbers (TON) would be achieved. This strategy is supported by the fact that ytterbium(II) shows far-reaching similarities to the heavy alkaline earth metal cations. Ytterbium(II)-mediated hydrophosphanylation of alkynes [126,127] does not involve a change of the oxidation state of Yb(II) and a similar reaction behaviour of calcium(II) and ytterbium(II) compounds seem possible. Catalytic activity affords easily accessible vacant coordination sites for substrate binding. This prerequisite can be achieved by bulky groups at the periphery of the molecule in order to shield the metal atom stabilizing low coordination numbers at the metal center. However, this protection strategy also hinders the coordination of substrate molecules to the metal atom and, hence, also hampers the reaction especially if the substrate becomes bulkier due to addition reactions. Therefore, we investigated the hydrophosphanylation of alkynes employing catalytic amounts of $[(thf)_4Ca(PPh_2)_2]$ (**8**) with potentially labile THF ligands. The bis(diphenylphosphanido) complexes of calcium are easily accessible, monomeric in solution and the solid state [18,19], and soluble in common organic solvents and, hence, resemble possible catalysts for hydrophosphanylation reactions. Contrary to this behaviour, monophenylphosphanides of the alkaline earth metals are oligomeric or polymeric in solution and the solid state and show poor solubility in common organic solvents [20].

The organocalcium chemistry represents a vastly developing branch of organometallic chemistry for many reasons [128-130, 4]. Uncommon structures of organocalcium derivatives such as bent molecules ($Ca[C(SiMe_3)_3]_2$) [131] or pyramidal calciates ($[Ca\{CH(SiMe_3)_2\}_3]^-$) [132] sparked interest in this compound class and beyond that in compounds of d^0 metals in general [133]. These investigations also initiated research regarding applications of these compounds for several reasons. Calcium is a non-toxic metal which is wide-spread and easily available. The heavy alkaline earth metal cations M^{2+} are isoelectronic to monovalent alkali metals and to three-valent elements of the scandium group. In addition, chemical similarities are also observed between calcium and ytterbium as well as strontium and europium in their oxidation states +2. Therefore, the heavy alkaline earth metals should be able to behave not only as a typical s-block element but also as an early transition metal. One of the most

attractive features of these elements is their catalytic activity. In the last very few years, the investigation of catalytic activity of calcium compounds raised the interest of several research groups. Calcium-mediated hydrophosphanylations of alkenes and diphenylacetylene [134] succeeded with sterically encumbered calcium complexes whereas the hydrophosphanylation of carbodiimides [135] was also catalyzed by alkaline earth metal bis[bis(trimethylsilyl)amides] of Ca, Sr, and Ba in the presence of secondary phosphanes. The hydrophosphanylation of *c*Hex-N=C=N-*c*Hex with $HPPh_2$ catalyzed by encumbered diketiminatocalcium complexes gave a yield of 85% after 28 hours whereas the use of $[(thf)_2Ca\{N(SiMe_3)_2\}_2]$ gave a higher yield already after a few hours. The use of calcium in catalyst systems tremendously gained on importance with the availability of soluble organocalcium complexes. We already tested the effectivity of $[(thf)_4Ca(PPh_2)_2]$ (**8**) as a catalyst for stereoselective hydrophosphanylation of diphenylbutadiyne with diphenylphosphane [136]. Also we extend our investigations on alkynes and butadiynes with different substituents in order to investigate the scope of this heterofunctionalization of alkynes. In a similar procedure, substituted butadiynes such as alkyl, aryl and trialkylsilyl can be converted catalytically and quantitatively into 1,4-diorganyl-1,4-bis(diphenylphosphanyl)buta-1,3-diene [137].

1.4. Synthesis and X-Ray Crystal Structure of $[(thf)_4Ca\{Fe_2(CO)_6(\mu\text{-}CO)(\mu\text{-}PPh_2)\}_2]$:

The easily accessible complex $[(thf)_4Ca(PPh_2)_2]$ shows an enormous reactivity as a catalyst in hydrophosphanylation reactions. The coordination behavior of the nucleophilic phosphanide anion offers various possibilities in coordination chemistry. The first reported dinuclear anion $[Fe_2(CO)_6(\mu\text{-}CO)(\mu\text{-}PPh_2)]^-$ (**A**$^-$) (Figure 1.9) [138], can be obtained from the reaction of $Na_2[Fe_2(CO)_8]$ with either R_2PCl [138, 139] or the nickel complex $[Ni(CO)_{4-n}(R_2PCl)_n]$ [140] yielding the sodium salt $Na[Fe_2(CO)_6(\mu\text{-}CO)(\mu\text{-}PR_2)]$. A similar reaction with the ammonium salt $(NEt_4)_2[Fe_2(CO)_8]$ leads to the formation of the corresponding $NEt_4[Fe_2(CO)_6(\mu\text{-}CO)(\mu\text{-}PR_2)]$ complex [141]. Heating of $NEt_4[HFe(CO)_3(PPh_3)]$ in ethanol gave $NEt_4[Fe_2(CO)_6(\mu\text{-}CO)(\mu\text{-}PPh_2)]$ with a rather poor yield [142]. The anion is isoelectronic to the neutral dinuclear mixed-metal complex $[FeCo(CO)_7(\mu\text{-}PR_2)]$ (**B**) which was obtained from the metalation of $(OC)_4Fe\text{-}PR_2H$ with $(\eta^3\text{-}C_3H_5)Co(CO)_3$ [143]. However, the latter complex is not isostructural to the homonuclear iron anion because the six-coordinate iron atom is coordinated to four terminally bound CO groups, the bridging phosphanide group and the cobalt atom, whereas the cobalt atom shows a coordination number of five where it is bonded to three terminally bound CO ligands, the iron atom and the phosphanide ligand. Oxidation of

the anion $[Fe_2(CO)_6(\mu\text{-}CO)(\mu\text{-}PR_2)]^-$ (**A**$^-$) with ferrocenium tetrafluoroborate produces the paramagnetic 33-electron complex $[Fe_2(CO)_6(\mu\text{-}CO)(\mu\text{-}PR_2)]$ (**A**) which has a structure similar to the heteronuclear FeCo compound [138, 139]. Protonation of $Na[Fe_2(CO)_6(\mu\text{-}CO)(\mu\text{-}PR_2)]$ yields $[Fe_2(CO)_6(\mu\text{-}CO)(\mu\text{-}H)(\mu\text{-}PR_2)]$ (**C**) with a bridging hydride ligand [140] and a Fe-Fe bond distance of 260.34(4) pm [144]. The exchange of sodium by bulky $[(Ph_3P)_2N]^+$ leads to the formation of an ion pair without short contacts between cation and anion [144]. The reaction of $NEt_4[Fe_2(CO)_6(\mu\text{-}CO)(\mu\text{-}PR_2)]$ with the PPh_3 adducts of CuI, AgI and AuCl yields the trinuclear complexes $[Fe_2(CO)_6(\mu\text{-}CO)(\mu\text{-}PR_2)\{\mu\text{-}M(PPh_3)\}]$ (**D**) with a Fe_2M triangle (M = Cu, Ag, Au) [145]. The formation of these heteronuclear clusters was verified by X-ray structure determinations [140,145,146].

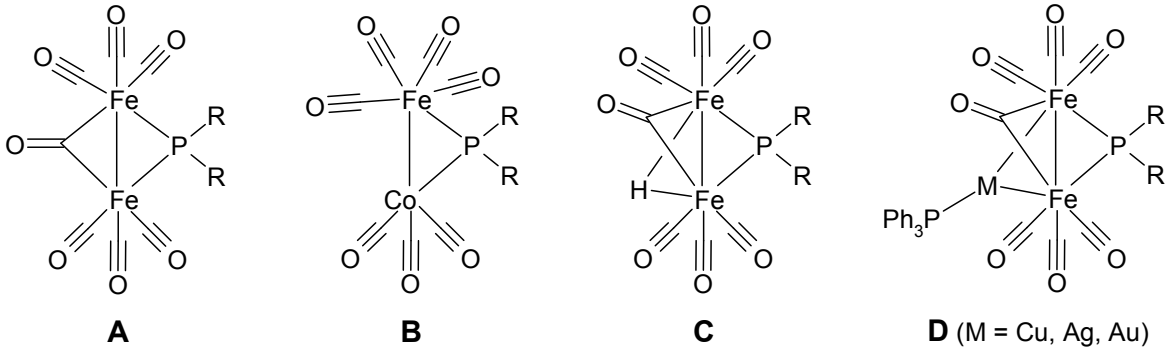


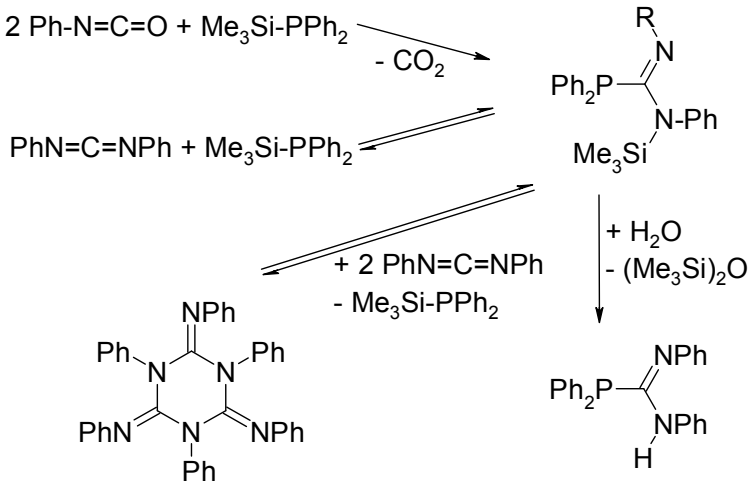
Figure 1.9: Schematic representations of A, B, C and D.

1.5. [Bis(tetrahydrofuran-*O*)-bis(1,3-dialkyl-2-diphenylphosphanyl-1,3-diazaallyl)calcium] – Synthesis and Crystal Structures of Catalytically Active Calcium Bis[phospha(III)guanidinates]:

Non-cyclopentadienyl organocalcium compounds are highly reactive compounds and therefore they are increasingly gaining the interest of many research groups [1, 128, 130b, 147]. This reactivity often leads to side reactions such as ether cleavage [1]. Non-redox active and very Lewis acidic cations in catalytic cycles have to be bound to hemilabile ligands in order to allow the creation of coordination gaps for substrate binding. Bulky groups at the periphery of the molecule shield the reactive metal center thus reducing side reactions. However, they also limit access of substrate molecules and often lower the catalytic reactivity. Complexes with hemilabile ligands such as THF molecules easily dissociate in solution. This reaction creates free coordination sites for substrate binding thus supporting catalytic activity.

We reported on hydrophosphanylation of carbodiimides with phosphanes yielding phospha(III)guanidines [148]. First reports on the synthesis of these phospha(III)guanidines dated 40 years ago. Itoh and co-workers [149] reported the reaction of $Me_3Si\text{-}PPh_2$ with

diphenylcarbodiimide and phenylisocyanate according to equation 6. Many years later Issleib *et al.* [150] reinvestigated the addition of trialkylsilyl substituted phosphanes to diphenylcarbodiimide. Thereafter Pudovic *et al.* [151] reported the reaction of primary and secondary phosphanes to PhN=C=NPh.



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N-Alkyl substituted phospha(III)guanidines were prepared from the stoichiometric reaction of $LiPPh_2$ with dialkylcarbodiimide and subsequent protolysis with $[HNEt_3]Cl$ [152]. The rich coordination behaviour of phospha(III)guanidinates was investigated in detail thereafter [152-155]. Oxidation of the phosphorus atom with chalkogenes led to the formation of phospha(V)guanidines [156,157]. Diphenylphosphane does not react with diisopropylcarbodiimide even at temperatures of 140°C. However, catalytic amounts (1-3 mol-%) of alkali metal bis(trimethylsilyl)amides are sufficient for quantitative conversion of these carbodiimides into the corresponding phospha(III)guanidines at room temperature [158]. The addition of $HPPh_2$ to diisopropylcarbodiimide can also be catalyzed at lanthanoide metal complexes with good yields [159]. Although good yields of 86% were also achieved with the yttrium complex, catalysis at scandium gave poor yields of only 15% under similar conditions [159]. Crimmin *et al.* [160] showed that sterically encumbered calcium complexes were also able to catalyze this reaction effectively. In addition, the molecular structures of the catalytically active calcium compounds were determined in order to compare these complexes with known complexes containing 1,3-diazaallyl fragments.

1.6. Synthesis and X-ray Structures of Calcium and Strontium Sulfur- or Selenium-Diphenylphosphinates of the Type $(L)_nM[E_2PPh_2]_2$ (E= S, Se) (L= THF).

Dithiophosphorus ligands $R_2PS_2^-$ (R= alkyl, aryl, alkoxy, aryloxy)), have been reported extensively in the literature [161] and have found several applications including lubricant oil additives [161,162] and extraction agents for separation procedures [163]. Also they exhibit a broad variety of coordination patterns leading to a wide range of molecular and supramolecular structures [161]; they can act as monodentate (monometallic monoconnective), iso- and anisobidentate (monometallic biconnective), or bridging (bimetallic biconnective and triconnective) ligands [164]. However, the chemistry of the heavier sulfur-homologues, the selenolates and tellurolates, is less documented and has only recently begun to attract more interest. This recent interest has been prompted by the desire for new syntheses of metal chalcogenolates which an be used as precursors to semiconducting selenides and tellurides, [165, 166].

Within this area, Davies *et al.* reported the synthesis and coordination chemistry of chalcogeno-phosphorus ligand systems, and has synthesized lithium selenophosphinite $[Ph_2PSeLi•TMEDA]_2$, diselenophosphinate $[Ph_2PSe_2Li•THF•TMEDA]$, and triselenophosphonate $[(c\text{-}C_6H_{11})\text{-}PSe_3Li_2•2TMEDA]$ complexes [167] (figure 1.10). These seleno-phosphorus ligands were shown to be easier to handle, more stable, and far less pungent than alkyl and aryl selenolates [167,168].

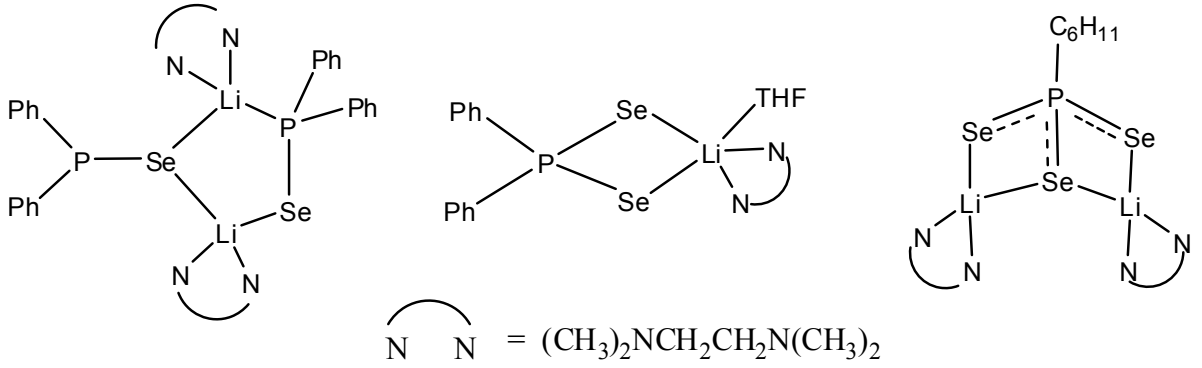


Figure 1.10: Lithium seleno-phosphorus complexes.

The indium(III) complexes of seleno-phosphorus ligands are of particular interest due to their potential applications as single-source precursors to indium selenide thin films [169a]. The europium complexes of seleno phosphorus ligands were used for the synthesis of nano-sized Eu-selenide with remarkable magneto-optical properties in the wavelength range shorter than 600 nm [169b]. Precedent to these applications, the reported use of dithiophosphinate and phosphinochalcogenoic amidate complexes such as $[Cd(S_2PR_2)_2]$ (R= CH_3 [170], C_2H_5 [171]), $Cd[N(SeP\textit{i}Pr_2)_2]_2$ [172] and $[M\{\textit{t}Bu_2P(Se)NR\}_2]$ (M= Zn, Cd, Cr, Mn, Fe, Co; R = *i*Pr,

c-C_6H_{11}) [173] in the area of the growth of semiconducting metal chalcogenide thin films using chemical vapor deposition processes are documented. Alkali metal complexes of the type $K(EPR_2BH_3)$ (E = O, S, Se, Te) have also been studied by Wagner *et al.* [174], and the alkali metal chalcogenoselenophosphinates $R_2P(X)Se^-$ (X = O, S, Se) were investigated by Kuchen and Hertel [175]. There are only few examples of main group metal complexes of the homologous diselenophosphinates or diselenophosphates, the only examples being the alkali metal complexes [Ph_2PSe_2Li·THF·TMEDA] [167], [$Na_2(Se_2PPh_2)_2$· THF•$5H_2O$] [176], and [$K_2(PhPSe_2)_2CH_2$] [177]. The former lithium complex was obtained by either treatment of *n*-BuLi with $HPPh_2$ and TMEDA, followed by the addition of selenium metal, or by the reaction of $HPPh_2$ with *n*-BuLi in THF solvent in the presence of TMEDA, followed by addition of one mole of grey selenium metal, forming $[Ph_2PSeLi·(TMEDA)]_2$, which was further treated with another mole of Se powder [167].

The diselenophosphinate complex, $Na_2[Ph_2PSe_2]_2$·THF·$5H_2O$, obtained from Ph_2PCl and inaccessible Na_xSe_y, has a polymeric structure consisting of a central core of fused and spiro Na_3O_3 rings [176]. One $Ph_2PSe_2^-$ acts as a unidentate ligand and the non-coordinated $Ph_2PSe_2^-$ anion contacts to the central polymeric core, *via* pairs of O-H· · ·Se hydrogen bonds (Figure 1.11).

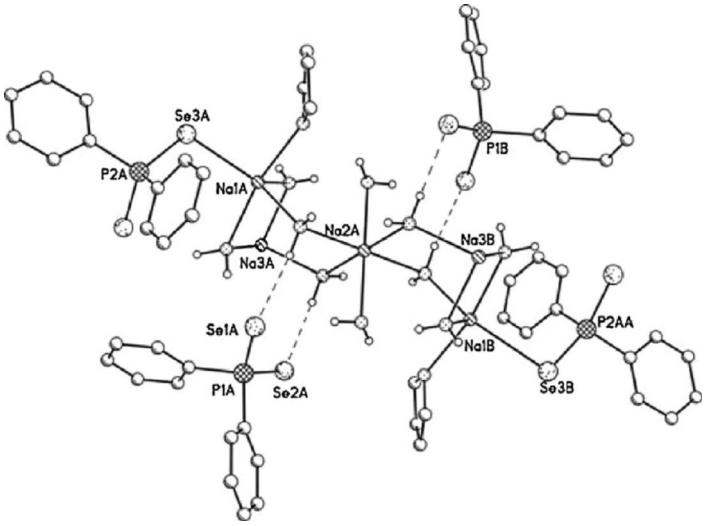


Figure 1.11. Hydrogen bonded Ph_2PSe_2 anions (adapted from Reference [176]).

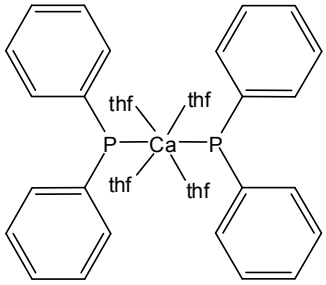
The reaction of potassium diphenylphosphanide with grey selenium metal in THF-toluene solution produced the complex $[K(Se_2PPh_2)(THF)_2]_2$ [169a]. Recently, the potassium diphenyldiselenophosphinate monohydrate, $K(Se_2PPh_2)·H_2O$, was prepared from potassium diphenylphosphane and selenium metal (THF, -30° C, 6 hr) [169b]. In addition, Gusarova *et*

al. reported that the secondary phosphane selenides, $R_2P(Se)H$, was reacted with elemental selenium and alkali metal hydroxides Se/MOH (M = Li, Na, K, Rb, Cs) in THF/EtOH system at ambient temperature to give cleanly and quantitatively diorganodiselenophosphinates of alkali metals [178a]. Antimony and indium dithiophosphinates $M(S_2PR_2)$ (M = Sb, R = Et; M = In, R = Me, Ph) were synthesized and characterized by Zukerman and Ionel [178b].

2. Experimental

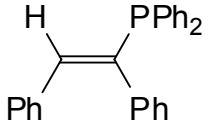
General remarks All manipulations were carried out in an argon atmosphere using standard Schlenk techniques. The solvents were dried according to common procedures and distilled under argon, deuterated solvents were dried over sodium, degassed, and saturated with argon. The ^{1}H and $^{13}C\{^{1}H\}$ NMR spectra were obtained on a Bruker AC 200 MHz and AC 400 MHz spectrometer. Mass spectra were obtained on a Finnigan MAT SSQ 710 and Finnigan MAZ95XL system. Peaks in the mass spectra were assigned by comparison of the observed isotopic patterns with the calculated ones. IR measurements were carried out using a Perkin-Elmer System 2000 FTIR. The IR spectra were taken as Nujol mulls between KBr windows, as KBr pellets or neat between KBr windows. Melting and decomposition points were measured with a Reichert-Jung apparatus type 302102 and are uncorrected.

2.1. Synthesis of calcium diphenylphosphanide $Ca(PPh_2)_2(THF)_4$ (8):



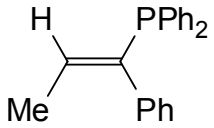
1.5 g of CaI_2 (5.1 mmol) was dissolved in 35 ml THF. A solution of potassium diphenylphosphanide (0.5 M, 20.4 ml, 10.2 mmol) in THF was dropwise added. The solution turned orange and KI precipitated. After 3 hours, KI was removed by filtration and the volume of the solution was reduced to half of the original volume and stored at -25 °C. 3.1 g of yellow crystals of $[(thf)_4Ca(PPh_2)_2]$ (4.44 mmol, 87%) were obtained. Physical data are in agreement with literature values [18].

2.2. Synthesis of 1,2-diphenyl-1-diphenylphosphanylethene (9a):



Diphenylacetylene (0.90 g, 5.05 mmol) was dissolved in 25 ml of THF and cooled to -78 °C. Diphenylphosphane (0.88 ml, 5.05 mmol) and 6 mol-% of $[(thf)_4Ca(PPh_2)_2]$ were added. The colourless reaction mixture turned orange immediately. This solution was warmed to room temperature and stirred for one hour. Volatiles were removed and the residue was washed twice with 25 ml of ether in order to obtain 1.42 g of colourless solid **9a** (3.9 mmol, 77%). Physical data are in agreement with literature values [181].

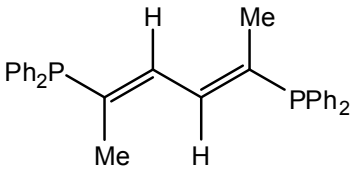
2.3. Synthesis of diphenyl-(1-phenylprop-1-enyl)phosphane (9b):



1-Phenylprop-1-yne (0.23 g, 1.98 mmol) in 15 ml of THF was cooled to -78 °C; 0.34 ml of $HPPh_2$ (0.37 g, 1.98 mmol) and 5 mol-% of $[(thf)_4Ca(PPh_2)_2]$ were added. The colourless solution turned yellow.

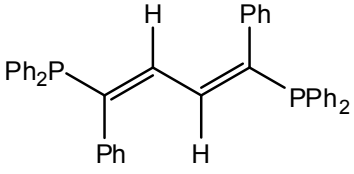
The reaction mixture was stirred at room temperature and then heated under reflux for additional 5 hours. Thereafter, all volatiles were removed in vacuum. The residue was dissolved in a mixture of methylene chloride and methanol. At -15 °C 0.51 g of colourless crystals of **9b** (1.69 mmol, 85%) precipitated. Physical data are in agreement with literature values [181, 182].

***2.4. Synthesis of 2,5-bis(diphenylphosphanyl)hexa-2,4-diene (10a)*:**



2,4-Hexadiyne (0.22 g, 2.82 mmol) in 18 ml of THF was cooled to -78 °C. 0.98 ml of $HPPh_2$ (1.0 g, 5.63 mmol) and 5 mol-% of $[(thf)_4Ca(PPh_2)_2]$ were added. The colourless solution turned yellow, the solution was stirred at room temperature for two hours and then under reflux for 4 hours. Reduction of the volume to half of original volume, addition of methanol and storage at -15 °C for one day led to the formation of colourless crystals of compound **10a** (1.03 g, yield 81%). *Physical data of **10a***: M.p. 129-132°C. MS (EI): 450 $[M]^+$ (1%), 389 $[M - PPh_2]^+$ (100%), 183 $[PPh_2 - 2\ H]^+$ (20%). ^1H NMR (400.25 MHz, $CDCl_3$): δ = 6.5 (CH, AA'XX' type, $^3J_{AA'}$ = 10.6 Hz, $^3J_{AX}$ = 13.1 Hz, $^4J_{AX'}$ = 0.7 Hz, $^5J_{XX'}$ = 0 Hz), 7.2-7.5 (phenyl). $^{13}C\{^1H\}$ NMR (50.322 MHz, $CDCl_3$, coupling constants to ^{31}P nuclei in brackets): δ = 23.7 (2C), 128.5 (2C, J= 4.7 Hz), 129.6 (2C, 9.5 Hz), 131.4 (4C), 131.9 (8C, 10.2 Hz), 133.3 (8C, 10.4 Hz), 135.3 (4C, 22.8 Hz). ^{31}P NMR (81.013 MHz, $CDCl_3$): δ = 10.8. IR (Nujol): 1957 w, 1882 w, 1761 w, 1660 w, 1583 m, 1568 w, 1377 vs, 1304 m, 1262 m, 1180 w, 1153 w, 1090 m, 1069 w, 1024 m, 997 w, 923 m, 980 w, 950 w, 916 w, 891 m, 802 m, 742 vs, 694 vs, 646 w, 554 w, 533 m, 515 s, 502 s, 475 s, 485 s, 459 w. Elemental analysis ($C_{30}H_{28}P_2$, 450,49): calc.: C 79.98, H 6.26; found: C 78.70, H 5.83.

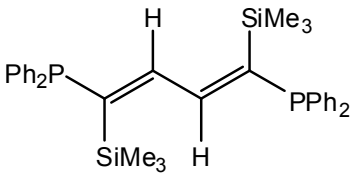
***2.5. Synthesis of 1,4-diphenyl-1,4-bis(diphenylphosphanyl)buta-1,3-diene (10b)*:**



A solution of 0.285 g of diphenylbutadiyne (1.41 mmol) in 15 ml of THF was cooled to -78°C. $HPPh_2$ (0.49 ml, 2.82 mmol) and 5 mol-% of $[(thf)_4Ca(PPh_2)_2]$ were added and the solution was stirred at room temperature for two hours. Then the volume was reduced to half of the original volume and cooled to -15°C. After one day colourless **10b** (0.72 g, 1.25 mmol, 89%) crystallized and was collected. *Physical data of **10b***: M.p. 216-220°C. MS (EI): 574 $[M]^+$ (1%), 389 $[M - PPh_2]^+$ (100%), 183 $[PPh_2 - 2\ H]^+$ (20%). ^1H NMR (400.25 MHz, $CDCl_3$): δ = 6.12 (CH, AA'XX' type, $^3J_{AA'}$ = 11.2 Hz, $^3J_{AX}$ = 6.5 Hz, $^4J_{AX'}$ = 0.5 Hz, $^5J_{XX'}$ = 0 Hz), 7.0-7.3 (phenyl). $^{13}C\{^1H\}$ NMR (50.328 MHz, $CDCl_3$, coupling

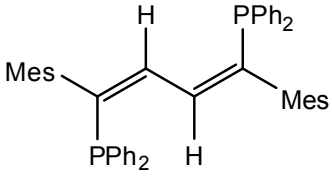
constants to ^{31}P nuclei in brackets): δ = 126.7 (2C), 127.9 (4C), 128.3 (8C, 6.6 Hz), 128.8 (4C), 129.1 (4C, 6.9 Hz), 133.8 (2C, 11.5 Hz), 134.2 (8C, 20.2 Hz), 135.2 (4C, 12.6 Hz), 139.3 (2C, 20.7 Hz), 143.6 (2C, 18.4 Hz). ^{31}P NMR (162.02 MHz, $CDCl_3$): δ = 7.8. IR (Nujol): 1584 w, 1434 s, 1180 w, 1090 m, 1071 m, 1026 m, 999 m, 923 m, 764 s, 741 vs, 694 vs, 600 s, 499 s. Elemental analysis ($C_{40}H_{32}P_2$, 574,630): calc.: C 83.61, H 5.61; found: C 81.13, H 5.73.

2.6. Synthesis of 1,4-bis(diphenylphosphanyl)-1,4-bis(trimethylsilyl)buta-1,3-diene (10c):



$HPPh_2$ (0.89 ml, 2.06 mmol) and 5 mol-% of $[(thf)_4Ca(PPh_2)_2]$ were added to a solution of 0.20 g of bis(trimethylsilyl)butadiyne (1.03 mmol) in 18 ml of THF at -78°C. The colourless solution turned red immediately. After stirring at room temperature for one hour and under reflux for additional 6 hours, the volume was reduced to half of the original volume. A few millilitres of methanol were added and the reaction mixture stored at -15°C. Colourless crystals of **10c** (0.46 g, 0.81 mmol, 79%) precipitated and were collected. *Physical data of **10c***: M.p. 93-96°C. MS (EI): 466 $[M]^+$ (1%), 389 $[M - PPh_2]^+$ (100%), 183 $[PPh_2 - 2\ H]^+$ (20%). ^1H NMR (200.13 MHz, $CDCl_3$): δ = 6.67 (CH, AA'XX' type, $^3J_{AA'}$ = 11.8 Hz, $^3J_{AX}$ = 16.9 Hz, $^4J_{AX'}$ = 0.2 Hz, $^5J_{XX'}$ = 0 Hz), 7.2-7.5 (phenyl). $^{13}C\{^1H\}$ NMR (100.643 MHz, $CDCl_3$, coupling constants to ^{31}P nuclei in brackets): δ = 128.9 (8C, 8.4 Hz), 129.9 (4C), 0.30 (2C), 134.7 (8C, 18.5 Hz), 131.8 (4C, 12.0 Hz), 133.1 (2C), 148.3 (2C, 10.1 Hz). ^{31}P NMR (81.01 MHz, $CDCl_3$): δ = 5.9. IR (KBr): 1617 w, 1584 w, 1554 w, 1434 s, 1407 w, 1307 m, 1250 vs, 1179 m, 1157 w, 1116 w, 1089 m, 1069 m, 1026 m, 999 m, 907 m, 857 vs, 841 vs, 741 vs, 696 vs, 633 s, 567 w, 554 s, 536 w, 501 vs. Elemental analysis ($C_{34}H_{40}P_2Si_2$, 466,80): calc.: C 72.05, H 7.11; found: C 71.91, H 6.79.

2.7. Synthesis of 1,4-bis(diphenylphosphanyl)-1,4-dimesitylbuta-1,3-diene (10d):



1,4-Dimesitylbuta-1,3-diyne (0.16 g, 0.56 mmol) was dissolved in 12 ml of THF at -78°C. $HPPh_2$ (0.19 ml, 1.12 mmol) and 5 mol- % of $[(thf)_4Ca(PPh_2)_2]$ were added, and the solution was stirred at room temperature for two hours. Then the volume was reduced to half of the original volume and 6 ml of methanol were added. After 2 days colourless crystals of **10d** were obtained at room temperature (0.28g, 76%). *Physical data of **10d***: M.p. 220-223°C. MS (EI): 658 $[M]^+$ (40%), 473 $[M - PPh_2]^+$ (60%), 183 $[PPh_2 - 2\ H]^+$ (80%). ^1H NMR (400.25 MHz, $CDCl_3$): δ = 7.6 (CH, AA'XX' type, $^3J_{AA'}$ = 6.0 Hz, $^3J_{AX}$ = 13.2 Hz, $^4J_{AX'}$ = 0.4 Hz, $^5J_{XX'}$ = 0 Hz), 7.2-7.5 (phenyl). $^{13}C\{^1H\}$ NMR (50.328 MHz, $CDCl_3$, coupling constants to ^{31}P nuclei in brackets): δ = 20.6 (2C), 21.3 (4C), 127.6 (8C, J= 3.3 Hz), 127.7 (8C, J= 3.4

Hz), 128.3 (4C), 133.7 (2C, J= 4.3 Hz), 133.8 (4C), 134.1 (4C, 4.6 Hz), 135.9 (4C), 136.5 (2C, 6.7 Hz), 137 (2C, 19.8 Hz), 138.8 (2C). ^{31}P NMR (81.013 MHz, $CDCl_3$): δ = -1.9. IR (KBr): 1953 w, 1888 w, 1810 w, 1611 m, 1584 m, 1569 w, 1478 vs, 1434 vs, 1375 m, 1307 w, 1263 w, 1203 w, 1185 w, 1157 w, 1094 m, 1069 w, 1027 m, 1000 w, 848 s, 811 w, 741 vs, 696 vs, 668 w, 609 w, 557 m, 504 s, 460 w. Elemental analysis ($C_{46}H_{44}P_2$, 658,79): calc.: C 83.86, H 6.73; found: C 83.08, H 6.61.

2.8. Synthesis of 3,6-bis(diphenylphosphanyl)-2,2,7,7-tetrametylocta-3,4-diene (12):

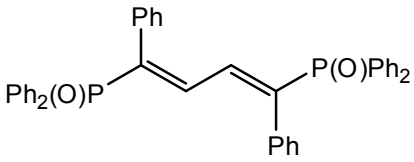
2,2,7,7-Tetramethyl-3,5-octadiyne (0.20 g, 1.23 mmol) was dissolved in 15 ml of THF at -78°C. $HPPh_2$ (0.43 ml, 2.46 mmol) and 5 mol- % of $[(thf)_4Ca(PPh_2)_2]$ were added, and the solution was stirred at room temperature for two hours. Then the volume was reduced to half of the original volume and 7 ml of methanol were added. After 3 days colourless crystals of **12** were obtained at room temperature (0.91g, 69%). *Physical data of **12***: M.p. 148-151°C. MS (EI): 534 $[M]^+$ (1%), 477 $[M\text{-}^tBu]^+$, 349 $[M - PPh_2]^+$ (100%), 293 $[349\text{-}^tBu]^+$ (20%), 183 $[PPh_2 – 2\ H]^+$ (60%). ^{1}H NMR (200.13 MHz, $CDCl_3$): δ = 1.02 (9H, s), 1.3 (9H, s), 2.88 (1H, dd, J = 8.7, 5.3 Hz), 4.68 (1H, ddd, J = 16.5, 8.3, 2.4 Hz), 6.92-7.43 (phenyl). $^{13}C\{^1H\}$ NMR (50.328 MHz, $CDCl_3$, coupling constants to ^{31}P nuclei in brackets): δ = 29.0 (J= 9.7), 29.4 (J= 10.2), 29.9 (J= 8.8), 35.2 (J= 16.5 Hz), 44.3.8 (J= 24.5), 85.5 (J= 16.7 Hz), 90.1 (J= 3.6 Hz), 127.5 (J= 7.3 Hz), 128.1 (J= 6.1 Hz), 128.4 (J= 6.9 Hz), 129.1, 132.6 (J= 17.9 Hz), 133.4 (J= 20.3 Hz), 135.2 (J= 21.0 Hz), 136.2 (J= 9.8 Hz), 138.5 (J= 12.3 Hz), 205.1 (J= 25.2 Hz). ^{31}P NMR (81.013 MHz, $CDCl_3$): δ = -2.3, -7.1. IR (KBr): 21090 w, 1928 m, 1662 m, 1585 m, 1477 vs, 1435 vs, 1392 m, 1362 s, 1309 w, 1261 vs, 1182 m, 1099 s, 1027 m, 803 vs, 741 vs, 725 w, 696 vs, 600 w, 541 s, 507m. Elemental analysis ($C_{36}H_{40}P_2$, 466,80): calc.: C 80.87, H 7.54; found: C 80.69, H 7.72.

2.9. Synthesis of 1,4-bis(diphenylphosphinyl)-1,4-bis(dimethyl)buta-1,3-diene (13a):

0.15 g of 2,5-bis(diphenylphosphanyl)hexa-2,4-diene was dissolved in 7ml of THF. H_2O_2 (30%, 0.067 ml) was added dropwise at 0 °C, the solution was stirred for one additional hour at room temperature. After reduction of the volume to half of the original volume, 3 ml of methanol were added. After 5 days colourless crystals of **13a** were obtained at room temperature (0.15g, 94%). *Physical data of **13a***: M.p. 212-215°C. MS (EI): 482 $[M]^+$ (100%), 281 $[M – OPPh_2]^+$ (40%), 201 $[OPPh_2]^+$ (60%). ^{1}H NMR (200.13 MHz, $CDCl_3$): δ = 7.13 (CH, AA'XX' type, $^3J_{AA'}$ = 11.2 Hz, $^3J_{AX}$ = 18.8 Hz, $^4J_{AX'}$ = 1.3 Hz, $^5J_{XX'}$ = 0 Hz), 7.4-7.7 (phenyl). $^{13}C\{^1H\}$ NMR (50.328 MHz, $CDCl_3$, coupling constants to

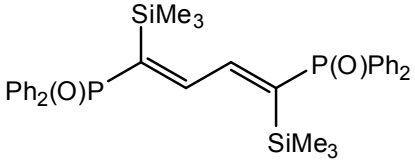
^{31}P nuclei in brackets): δ = 128.5 (8C, 4.6 Hz), 128.9 (4C, 6.0 Hz), 129.5 (4C), 14.1 (2C), 132.1 (8C, 22.4 Hz), 135.1 (2C, 2.9 Hz), 136.9 (2C). ^{31}P NMR (81.01 MHz, $CDCl_3$): δ = 36.2. IR (KBr): 1986 w, 1907 w, 1827 w, 1783 w, 1626 m, 1589 m, 1573 w, 1461 vs, 14340 vs, 1378 vs, 1312 m, 1244 w, 1169 vs, 1118 vs, 1093 w, 1071 m, 1026 m, 996 s, 966 s, 907 w, 861 w, 752 s, 723 vs, 697 vs, 662 s, 621 w, 590 w, 545 vs, 504 w. Elemental analysis ($C_{30}H_{28}O_2P_2$, 482,49): calc.: C 74.68, H 5.85; found: C 74.44, H 5.83.

2.10. Synthesis of 1,4-diphenyl-1,4-bis(diphenylphosphinyl)buta-1,3-diene (13b):



1,4-Diphenyl-1,4-bis(diphenylphosphanyl)buta-1,3-diene (0.1 g) was dissolved in 8ml of THF. H_2O_2 (30%, 0.036 ml) was added dropwise to the solution at 0 °C. Then the solution was stirred for one additional hour at room temperature. After reduction of the volume to half of original volume, then add 4 ml methanol. After 6 days colourless crystal of **13b** were obtained at room temperature (0.098g, 93%). *Physical data of **13b***: M.p. 276-279°C. MS (EI): 606 $[M]^+$ (1%), 405 $[M - OPPh_2]^+$ (100%), 201 $[OPPh_2]^+$ (20%). ^{1}H NMR (200.13 MHz, $CDCl_3$): δ = 6.73 (CH, AA'XX' type, $^3J_{AA'}$ = 10.9 Hz, $^3J_{AX}$ = 19.2 Hz, $^4J_{AX'}$ = 1.1 Hz, $^5J_{XX'}$ = 0 Hz), 7.2-7.5 (phenyl). δ = 128.0 (4C), 128.3 (4C), 128.4 (2C), 129.5 (8C, 20 Hz), 131.9 (8C, 9.4 Hz), 134.1 (4C, 8.1 Hz), 137.8 (4C), 138.2 (2C, 14.3Hz), 141.9 (2C), 143.6 (2C). ^{31}P NMR (81.01 MHz, $CDCl_3$): δ = 33.55. IR (KBr): 1968 w, 1901 w, 1825 w, 1590 m, 1574 w, 1552 w, 1487 s, 1437 vs, 1311 m, 1279 w, 1192 vs, 1117 vs, 1100 s, 1072 m, 1029 m, 998 m, 935 w, 900s, 851 w, 768 m, 752 m, 724 vs, 701 vs, 631 w, 617 w, 603 s, 584 w, 566 m, 548 vs, 507 s.. Elemental analysis ($C_{40}H_{32}O_2P_2$, 606,63): calc.: C 79.20, H 5.32; found: C 79.10, H 5.13.

2.11. Synthesis of 1,4-bis(diphenylphosphinyl)-1,4-bis(trimethylsilyl)buta-1,3-diene (13c):

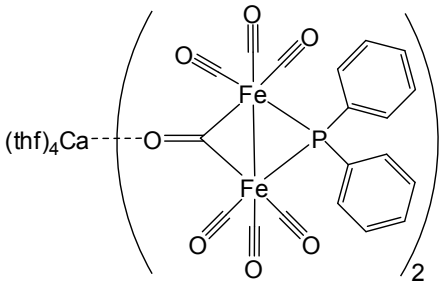


1,4-Bis(diphenylphosphanyl)-1,4-bis(trimethylsilyl)buta-1,3-diene (0.03 g) was dissolved in 7ml of THF. H_2O_2 (30%, 0.01 ml) was added dropwise to the solution at 0 °C, then the solution was stirred for one hour at room temperature. After reduction of the volume to 3 ml, 3 ml of methanol were added. After 5 days colourless crystals of **13c** were obtained at room temperature (0.029g, 92%). *Physical data of* **13c**: M.p. 182-185°C. MS (EI): 598 $[M]^+$ (1%), 397 $[M - OPPh_2]^+$ (100%), 201 $[OPPh_2]^+$ (20%). ^{1}H NMR (200.13 MHz, $CDCl_3$): δ = 7.03 (CH, AA'XX' type, $^3J_{AA'}$ = 11.4 Hz, $^3J_{AX}$ = 30.2 Hz, $^4J_{AX'}$ = 1.1 Hz, $^5J_{XX'}$ = 0 Hz), 7.4-7.7 (phenyl). $^{13}C\{^1H\}$ NMR (50.328 MHz, $CDCl_3$, coupling constants to ^{31}P nuclei in brackets): δ = 128.7 (8C, 12.3 Hz), 131.7 (8C, 7.3 Hz), 133.4 (4C), 147.4 (4C), 148.7 (2C), 151.3 (2C, 29.7 Hz), 0.7 (2C). ^{31}P NMR

(81.01 MHz, $CDCl_3$): δ = 40.8. IR (KBr): 1963 w, 1900 w, 1821 w, 1711 w, 1590 m, 1483 s, 1437 vs, 1407 w, 1309 m, 1250 vs, 1189 vs, 1118 vs, 1100 s, 1070 m, 1026 m, 998 m, 898 s, 875 m, 842 vs, 746 s, 722 s, 696 vs, 635 s, 617 w, 570 s, 538 vs. Elemental analysis ($C_{34}H_{40}O_2P_2Si_2$, 598,80): calc.: C 68.20, H 6.73; found: C 67.24.10, H 6.59.

2.12. Synthesis of [(thf)$_4$Ca{Fe$_2$(CO)$_6$(μ-CO)(μ-PPh$_2$)}$_2$] (14):

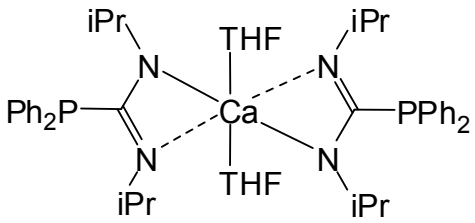
Method A: A solution of 0.16 g of [(thf)$_4$Ca(PPh$_2$)$_2$] (0.229 mmol) in 15 ml of THF was added dropwise at 0°C to a solution of 0.17 g of $Fe_2(CO)_9$ (0.458 mmol) in 35 ml of THF. The colour of the solution changed from yellow to red. After complete addition, the solution was warmed to r.t. and stirred for several hours. After reduction of the volume and storage at -25°C, 0.23 g of red crystals of **14** (0.17 mmol, 77%) precipitated.



Method B: A solution of 0.21 g of [(thf)$_4$Ca(PPh$_2$)$_2$] (0.30 mmol) in 15ml of THF was added dropwise at 0°C to a solution of $Fe_3(CO)_{12}$ (0.30 g, 0.60 mmol) in 35 ml of THF. The colour of the solution changed from yellow to red. After complete addition, the solution was warmed to r.t and stirred for several hours. In order to complete the reaction, the solution was heated under reflux for 4 h. After reduction of the volume and storage at -25°C, 0.29 g of red crystals of **14** (0.22 mmol, 73%) precipitated. Physical data of **14**: M.p. 206-209°C (dec.). Elemental analysis ($C_{54}H_{52}CaFe_4O_{18}P_2$, 1314.38): Calc.: C 49.34, H 3.99; found: C 48.36, H 4.88. ^{1}H NMR: δ (ppm) = 1.73 and 3.58 (THF), 7.1-7.8 (phenyl). ^{31}P{^{1}H} NMR: δ (ppm) = 127.9. IR: 3051 w (C-H); 2027 s, 1979 s, 1951 s, 1934 vs, 1915 s, 1770 m (sh, broad, μ-CO), 1596 s, 1460 vs, 1377 s, 1305 w, 1260 sh, 1170 w, 1128 w, 1093 w, 1026 m, 998 w, 917 w, 874 m, 742 m, 722 m, 698 m, 659 m, 633 m, 625 w, 608 w, 592 s, 548 w, 511 m. MS (DEI, m/z, %): 28 (CO, 38), 42 (100), 72 (THF, 56), 78 (C_6H_6, 25), 242 ($HFePPh_2$, 39), 482 ($Fe_2P_2Ph_4$, 37), 510 ($Fe_2P_2Ph_4CO$, 43), 566 ($Fe_2P_2Ph_4C_3O_3$, 6), 622 ($Fe_2P_2Ph_4C_5O_5$, 20), 650 ($Fe_2P_2Ph_4C_6O_6$, 5).

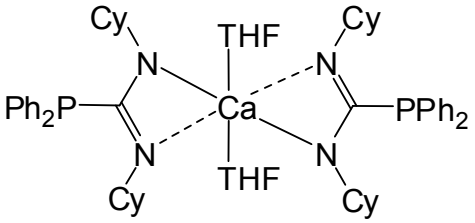
***2.13. Synthesis of [(thf)$_2$Ca{iPrNC(PPh$_2$)N^{i}Pr}$_2$] (15)*:**

Method A: A solution of 0.35 g of [(thf)$_4$Ca(PPh$_2$)$_2$] (0.51 mmol) and 0.13 g of diisopropylcarbodiimide (1.01 mmol) in 30 ml of THF was stirred at -78°C for one hour and then one day at r.t. Reduction of the volume to a third of the original volume and addition of 10 ml of pentane led to the precipitation of 0.33 g of **15** (82%).



Method B: A solution of 0.32 g of diisopropylcarbodiimide (2.54 mmol) in 20 ml of THF was added dropwise at -78°C to a 0.5 M solution of $KPPh_2$ (2.54 mmol) in THF. After warming to r.t. and stirring over night, 0.37 g of anhydrous CaI_2 (1.27 mmol) were added and the mixture stirred for 24 h at r.t. The volume of this yellow solution was reduced to 10 ml and 10 ml of pentane were added. 0.72 g of colourless crystals of **15** (71%) precipitated within a few days. Physical data: M.p. 160-163°C (dec.). Elemental analysis ($C_{46}H_{64}CaN_4O_2P_2$, 807.05): calc.: C 68.46, H 7.99, N 6.94; found: C 66.72, H 7.95, N 6.35. IR: 1599 s, 1584 m, 1550 w, 1460 vs, 1370 s, 1360 s, 1322 vs, 1301 m, 1220 w, 1174 vs, 1127 m, 1117 m, 1089 w, 1069 m, 1038 s, 995 s, 901 m, 818 m, 743 vs, 696 vs, 630 m, 608 m, 553 w, 504 s, 482 s. ^{1}H NMR ([D$_8$]THF, 25°C): δ 0.73 (d, Me, ^{3}J(H,H) = 6 Hz), 3.92 (sep, CH_{Pr}, ^{3}J(H,H) = 6 Hz), 7.21 (m, Ph, p- and o-CH), 7.58 (m, Ph, m-CH), 1.74 and 3.62 (THF). ^{31}P{^{1}H} NMR ([D$_8$]THF, 25°C): δ -20.6.

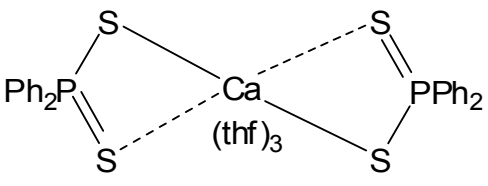
***2.14. Synthesis of [(thf)$_2$Ca{CyNC(PPh$_2$)NCy}$_2$] (16)*:**



Method A: In a similar procedure as described above, a solution of 0.51 g of [(thf)$_4$Ca(PPh$_2$)$_2$] (0.73 mmol) and of 0.30 g of dicyclohexylcarbodiimide (1.46 mmol) in 30 ml of THF was prepared. After stirring for a day at r.t. the volume was reduced to a third and 10 ml of pentane were added. Yellow crystals of **16** (0.58 g, 82%) precipitated within a few days.

Method B: In a similar procedure as described above 0.72 g of dicyclohexycarbodiimide (3.49 mmol) in 20 ml of THF was dropped at -78°C into a 0.5 M solution of $KPPh_2$ in THF (3.47 ml). After stirring over night 0.51 g of anhydrous CaI_2 (1.75 mmol) were added and the reaction mixture stirred one day at r.t. Reduction of the volume to 10 ml and addition of 10 ml of pentane led to the crystallization of 1.41 g of yellow **16** (83%). Physical data: M.p. 190-193°C (dec.). Elemental analysis ($C_{58}H_{80}CaN_4O_2P_2$, 967.31): calc.: C 72.02, H 8.34, N 5.79; found: C 70.77, H 8.26, N 5.59. IR: 1598 s, 1583 s, 1449 vs, 1366 s, 1343 s, 1303 w, 1253 m, 1218 m, 1180 m, 1155 s, 1100 s, 1068 m, 1044 s, 1027 m, 983 s, 887 s, 849 m, 802 w, 741 vs, 695 vs, 613 m, 593 m, 561 w, 525 m, 503 w, 487 s. ^{1}H NMR ([D$_8$]THF, 25°C): δ 0.9 – 1.9 (m, Cy), 7.2 – 7.4 (m, Ph), 1.74 and 3.62 (THF). ^{31}P{^{1}H} NMR ([D$_8$]THF, 25°C): δ -21.5.

2.15. Synthesis of Ca[S$_2$-PPh$_2$]$_2$(THF)$_3$ (17):

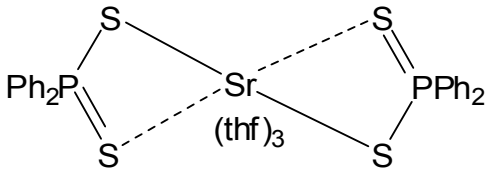


Method A: 6.6 ml (0.5 M, 3.3 mmol) of $KPPh_2$ in THF was added to a suspension of S_8 (0.21g, 6.6 mmol) in 10 ml THF and stirred for 6 hours under argon atmosphere at -35 °C. The solution was stirred over night. CaI_2 (0.48g, 1.65 mmol) was

added to the solution at -78 °C and stirred for 2 hours at room temperature. The mixture was filtered to remove the potassium iodide. Then reduction of the volume to half of the original volume at -25 °C led to colourless crystals of **17** (0.98g, 80%).

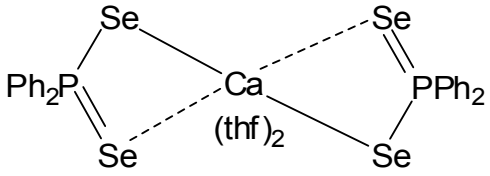
Method B: 0.342g (0.96mmol) of $Ca(N(SiMe_3)_2)_2$ was dissolved in 18ml of THF at -78 °C, 0.48g (1.92mmol) of diphenyldithiophosphonic acid in 10 ml of THF was added dropwise to the solution of $Ca(N(SiMe_3)_2)_2$. The solution was stirred overnight. Reduction of the volume to 7 ml and addition of pentane at -25 °C led to colourless crystals of **17** after 2 weeks (0.57g, 79%). Physical data: M.p. 254-257°C (dec.). Elemental analysis ($C_{36}H_{44}CaO_3P_2S_4$, 755.02): calc.: C 57.27, H 5.87, S 16.99; found: C 57.04, H 5.84, S 17.25. IR: 1585 w, 1569 w, 1460 vs, 1377 vs, 1305 s, 1173 m, 1156 m, 1096 s, 1068 w, 1026 s, 999 w, 917 w, 873 m, 744 s, 703 s, 666 m, 653 s, 613 s, 566 vs, 491 m, 483 m. ^{1}H NMR ([D$_8$]THF, 200.13 MHz): δ 7.28 (m, Ph, m- and p-CH), 8.06 (m, Ph, o-CH), 1.74 and 3.62 (THF). ^{13}C NMR (50.32 MHz, d$_8$-THF): δ = 143.9 d (C_i, $^1J_{PC}$ = 78.0 Hz); δ = 131.1 d (C_o, $^2J_{PC}$ = 11.5 Hz); δ = 129.8 s (C_p), δ = 127.9 d (C_m, $^3J_{PC}$ = 12.5 Hz), δ = 67.1, 25.2 (THF). ^{31}P{^{1}H} NMR ([D$_8$]THF, 81.013 MHz): δ 61.5.

2.16. Synthesis of $Sr[S_2\text{-}PPh_2]_2(THF)_3$ (18):



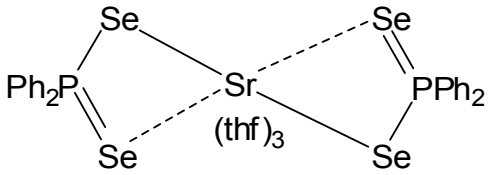
2.76 ml (0.5 M, 1.38 mmol) of $KPPh_2$ in THF was added to a suspension of S_8 (0.09 g, 2.76 mmol) in 10 ml of THF and stirred for 6 hours under an argon atmosphere at -35 °C. The solution was stirred overnight. $SrI_2(thf)_5$ (0.483 g, 0.688 mmol) was added to this solution at -35 °C, and stirring was continued for 2 hours at room temperature. The mixture was filtered to remove potassium iodide and then the volume was reduced to half of the original volume. 3 ml of toluene was added at -25 °C and led to the precipitation of colourless crystals of **18** after 24 h (0.39 g, 78%). Physical data: M.p. 107-110°C (dec.). Elemental analysis ($C_{36}H_{44}SrO_3P_2S_4$, 802.56): calc.: C 53.88, H 5.53, S 15.98; found: C 53.04, H 5.48, S 15.87. IR: 1634 w, 1457 vs, 1377 vs, 1305 s, 1173 m, 1156 m, 1096 s, 1068 w, 1026 s, 998 w, 917 w, 874 m, 745 s, 721 w, 702 s, 662 m, 650 s, 612 s, 562 vs, 491 m, 482 m. ^{1}H NMR ([D$_8$]THF, 200.13 MHz): δ 7.25 (m, Ph, m- and p-CH), 8.02 (m, Ph, o-CH), 1.74 and 3.62 (THF). ^{13}C NMR (50.32 MHz, d$_8$-THF): δ = 144.2 d (C_i, $^1J_{PC}$ = 79.2 Hz); δ = 131.1 d (C_o, $^2J_{PC}$ = 11.5 Hz); δ = 129.8 s (C_p), δ = 127.9 d (C_m, $^3J_{PC}$ = 12.6 Hz); δ = 67.1, 25.2 (THF). ^{31}P{^{1}H} NMR ([D$_8$]THF, 81.013 MHz): δ 61.48.

2.17. Synthesis of Ca[Se$_2$-PPh$_2$]$_2$(THF)$_2$ (19):



$Ca(PPh)_2(THF)_4$ (0.17 g, 0.24 mmol) was added dropwise to a suspension of Se (0.15 g, 1.89 mmol) in THF (8 ml) at -78 °C. The mixture was stirred for additional 6 hours at the same temperature and then allowed to warm to room temperature with constant stirring to afford a clear yellow solution. Then stirring was interrupted in order to allow excess selenium to settle. Thereafter the solution was filtered. The volume of the filtrate was reduced to 5 ml. Addition of toluene (4 ml) led to colourless crystals of **19** after 3 days (0.17 g, 81%). Physical data: M.p. 198-202°C (dec.). Elemental analysis ($C_{32}H_{36}CaO_2P_2Se_4$, 755.02): calc.: C 44.15, H 4.17; found: C 42.68, H 4.44. IR: 1607 w, 1571 w, 1458 vs, 1377 vs, 1305 m, 1261 m, 1180 w, 1154 w, 1089 s, 1067 w, 1026 s, 918 m, 873 m, 800 m, 743 s, 689 s, 618 m, 543 vs, 518 vs, 472 s. ^{1}H NMR ([D_8]THF, 200.13 MHz): δ 7.25 (m, Ph, m- and p-CH), 8.06 (m, Ph, o-CH), 1.74 and 3.62 (THF). ^{13}C NMR (100.65 MHz, d_8-THF): δ = 142.0 d (C_i, $^1J_{PC}$ = 122.8 Hz); δ = 131.8 d (C_o, $^2J_{PC}$ = 11.6 Hz); δ = 130.0 s (C_p), δ = 127.9 d (C_m $^3J_{PC}$ = 12.5 Hz); δ = 67.1, 25.2 (THF). ^{31}P{^{1}H} NMR ([D_8]THF, 81.013 MHz): δ 21.8 (s + d satellites, $^1J_{PSe}$ = 574.1 Hz).

2.18. Synthesis of Sr[Se$_2$-PPh$_2$]$_2$(THF)$_3$ (20):



2.41 ml (0.5 M, 1.21mmol) of $KPPh_2$ in THF was added to a suspension of Se (0.19 g, 2.42 mmol) in 10 ml of THF and stirred for 6 hour under an argon atmosphere at -35 °C, then stirring was maintained at room temperature over night. $SrI_2(thf)_5$ (0.423 g, 0.603 mmol) was added to this solution at -35 °C. Then the reaction mixture was stirred for 2 hours at room temperature. The mixture was filtered to remove potassium iodide and then the volume was reduced to half of the original volume. Addition of 3 ml of hexane at -25 °C led to colourless crystals of **20** after 3 days (0.49g, 82%). Physical data: M.p. 118-121°C (dec.). Elemental analysis ($C_{36}H_{44}SrO_3P_2Se_4$, 990.14): calc.: C 43.67, H 4.48; found: C 42.40, H 4.12. IR: 1608 w, 1571 w, 1456 vs, 1378 vs, 1341 w, 1304 s, 1177 m, 1156 w, 1091 s, 1067 w, 1030 s, 998 w, 918 m, 876 m, 746 s, 689 s, 618 m, 538 m, 516 vs, 467 s. ^{1}H NMR ([D_8]THF, 25°C): δ 7.23 (m, Ph, m- and p-CH), 8.03 (m, Ph, o-CH), 1.74 and 3.62 (THF). ^{13}C NMR (50.32 MHz, d_8-THF): δ = 142.0 d (C_i, $^1J_{PC}$ = 61.4 Hz); δ = 131.8 d (C_o, $^2J_{PC}$ = 11.9 Hz); δ = 129.9 s (C_p), δ = 127.8 d (C_m $^3J_{PC}$ = 12.5 Hz); δ = 67.1, 25.2 (THF). ^{31}P{^{1}H} NMR ([D_8]THF, 81.013 MHz): δ 22.4 (s + d satellites, $^1J_{PSe}$ = 633.6 Hz).

3. Results and Discussion:

3.1. Synthesis of $Ca(PPh_2)_2(THF)_4$ (8):

The strontium and barium bis(diphenylphosphanides) were prepared by metallation of $HPPh_2$ with the metals in THF according to equation (7) similar to the synthesis of the diphenylamides [179] and aryl-(trimethylsilyl)amides [180] of these metals. The larger radius of barium led to a higher THF content of the complex. Calcium did not possess the capability to deprotonate the secondary phosphane. Therefore, the metathesis reaction of CaI_2 with $KPPh_2$ offered an alternative due to the insolubility of KI in THF according to equation (8) [18].

$$M + 2HPPh_2 \xrightarrow{THF} (thf)_nM(PPh_2)_2 + H_2 \qquad (7)$$

M = Sr, n = 4 ,
M = Ba, n = 5

$$CaI_2 + 2\ KPPh_2 \xrightarrow{THF} (thf)_4Ca(PPh_2)_2 + 2\ KI \qquad (8)$$

8

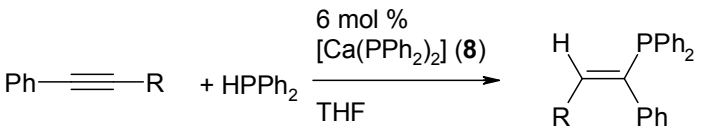
The metallation of $HPPh_2$ with $(thf)_4Ca(Ph)PPh_2$ also offered access to compound **8**. The synthesis of calcium bis(diphenylphosphanide) did not succeed via dismutation of $(thf)_4Ca(Ph)PPh_2$ in analogy to diphenylcalcium because heteroleptic $(thf)_4Ca(Ph)PPh_2$ is stable in THF. Also the addition of diethylether could not initiate a dismutation reaction and the formation of **8**, but metallation of $HPPh_2$ with this complex yielded homoleptic $Ca(PPh_2)_2$.

3.2. Synthesis of Vinylphosphanes *via* Calcium-Mediated Hydrophosphanylation of Alkynes and Butadiynes:

We investigated the hydrophosphanylation of alkynes employing catalytic amounts of $[(thf)_4Ca(PPh_2)_2]$ (**8**) with potentially labile THF ligands. The bis(diphenylphosphanido) complexes of calcium are easily accessible, monomeric in solution and the solid state [18, 19] and soluble in common organic solvents and, hence, resemble possible catalysts for hydrophosphanylation reactions. Contrary to this behaviour, monophenylphosphanides of the alkaline earth metals are oligomeric or polymeric in solution and the solid state and show poor solubility in common organic solvents [20]. In order to test the effectivity of $[(thf)_4Ca(PPh_2)_2]$

(**8**) as a catalyst for the hydrophosphanylation reactions, we already tested that $[(thf)_4Ca(PPh_2)_2]$ (**8**) served as highly effective precataylst for stereoselective intermolecular hydrophosphanylation of diphenylethyne and diphenylbutadiyne with diphenylphosphane [136]. Based on this work, we intended to prepare new NUPHOS ligands *via* hydrophosphanylation of phenylmethylethyne and of butadiynes with different substituents such as alkyl, aryl, and trialkylsilyl in order to investigate the scope of this heterofunctionalization of alkynes. Due to their high acidity, hydrogen atoms at the alkyne moieties lead to side reactions and are not suitable as substituents.

The calcium complex (20 mol %) with a bulky β-diketiminato ligand catalyzed the hydrophosphanylation of diphenylethyne and a nearly quantitative conversion was achieved after 13 hours at 75°C in $[D_6]$benzene [134]. In less than two hours *trans*-1,2-diphenyl-1-diphenylphosphanylethene (**9a**) formed quantitatively at room temperature in a similar reaction with catalytic amounts of $[(thf)_4Ca(PPh_2)_2]$ (**8**) (6 mol %) according to equation 9. The hydrophosphanylation of 1-phenylprop-1-yne proceeded regio- and stereoselectively and yielded diphenyl-(1-phenylprop-1-enyl)phosphane (**9b**).



(9)

R = Ph (**9a**), Me (**9b**)

These vinylphosphanes are well-known substances and a comparison of the NMR parameters verified the formation of **9a** [181] and **9b** [182, 183]. The molecular structures of the *cis*- and *trans*-isomers of **9a** show distortions of the bond angles as expected for sterically strained alkenes [183]. Molecular structure and numbering scheme of **9b** are shown in Figure 3.1. Selected structural parameters are compared in Table 1 with literature values [183] of *cis*- and *trans*-1,2-diphenyl-1-diphenylphosphanylethene (**9a**) and of (**I**) [184]. In **9b** all P-C bond lengths are very similar and the phosphorus atom is in a pyramidal coordination sphere (angle sum at P1 305.9°) excluding any π-interaction with the vinyl unit. Steric strain between the phenyl group at C2 and the PPh_2 substituent leads to an enhancement of the C1-C2-C3 angle whereas the P1-C1-C2 angle adopts a characteristic value of a sp^2-hybridized carbon atom. Substitution of the methyl group of C9 by a hydrogen atom (as in compound **I**) leads to an extremely large P1-C1-C2 angle of more than 130° suggesting that the methyl group in **9b** cannot get out of the way as easily as a hydrogen atom due to the neighbourhood of the C2-

bound H atom. The C1=C2 double bond length remains unaffected by the steric strain in all these derivatives.

Figure 3.1: Molecular structure and numbering scheme of *cis*-1-phenyl-2-diphenylphosphanyl-1-propene (**9b**). The ellipsoids represent a probability of 40%, H atoms are omitted for clarity reasons. Selected structural data are listed in Table 3.1.

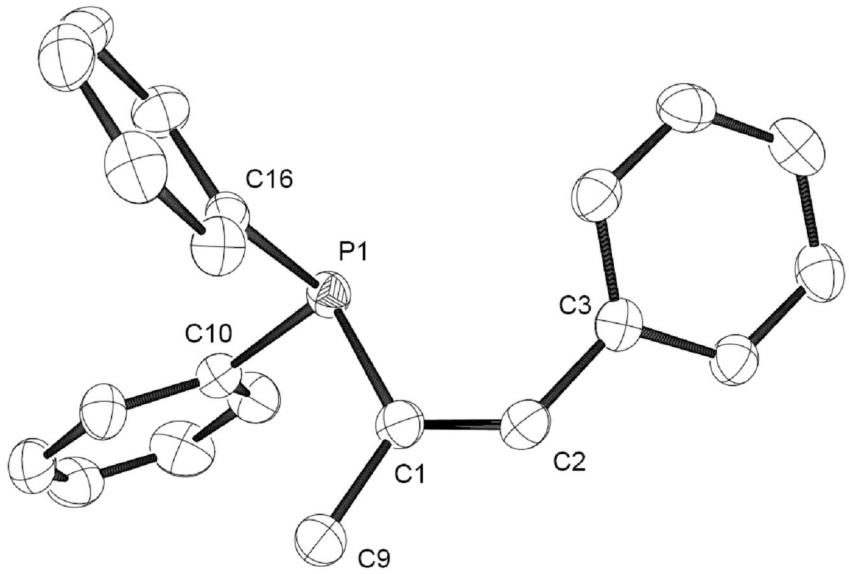
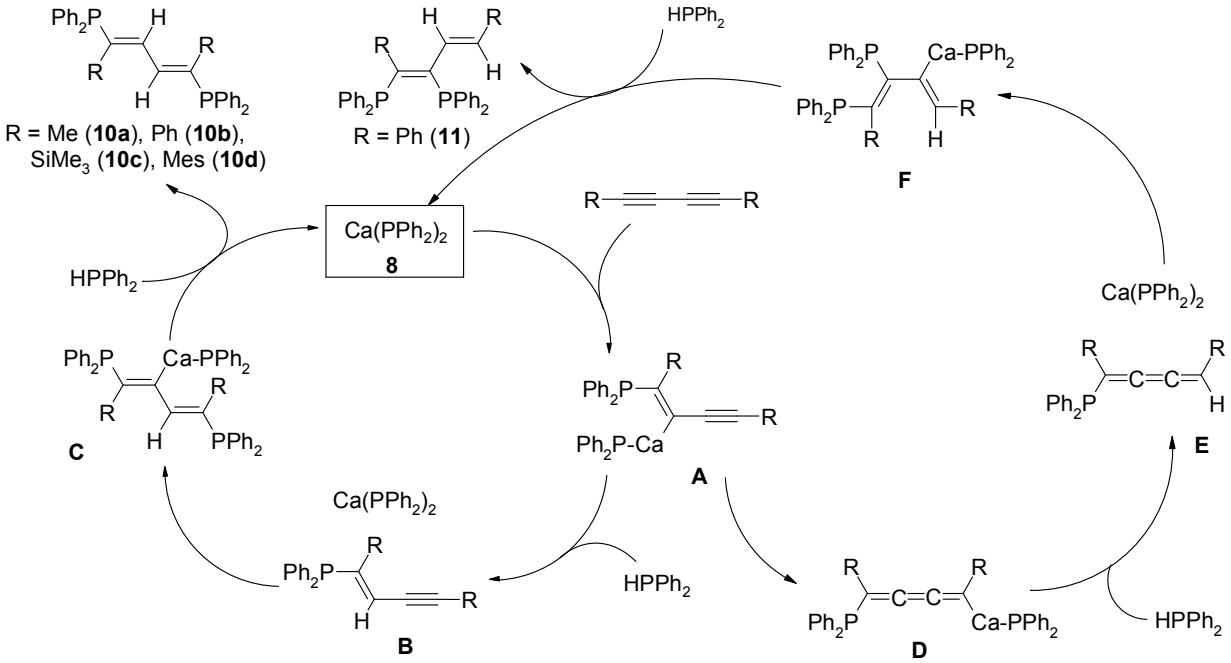


Table 3.1: Comparison of selected structural data of *cis*- and *trans*-1,2-diphenyl-1-diphenylphosphanylethene (**9a**) [182], *cis*-1-phenyl-2-diphenylphosphanylethene (**I**) [184], and *cis*-1-phenyl-2-diphenylphosphanyl-1-propene (**9b**).

	***Cis*-9a**	***Trans*-9a**	***Cis-I***	***Cis*-9b**
P1-C1	185.1(2)	183.7(1)	181.4(2)	184.0(2)
P1-C10	183.4(2)	183.7(2)	184.1(2)	184.2(2)
P1-C16	183.8(2)	183.3(2)	183.9(1)	183.7(2)
C1-C2	133.8(2)	133.5(2)	133.9(2)	133.8(2)
C1-C9	149.2(2)	150.1(2)	-	151.1(2)
C2-C3	148.4(2)	147.5(2)	146.7(2)	147.8(2)
C1-P1-C10	99.07(7)	102.09(7)	102.77(7)	101.06(7)
C1-P1-C16	104.35(7)	105.08(6)	99.78(7)	102.67(7)
C10-P1-C16	102.78(7)	100.39(6)	98.57(6)	102.14(7)
P1-C1-C2	119.5(1)	123.8(1)	130.6(1)	120.5(1)
P1-C2-C9	120.8(1)	112.3(1)	-	119.8(1)
C2-C1-C9	119.2(1)	123.8(1)	-	119.6(2)
C1-C2-C3	127.9(2)	129.3(1)	131.1(2)	129.4(2)

The reaction of $HPPh_2$ with butadiynes in the presence of catalytic amounts of **8** (approx. 5 mol %) produced 1,4-bis(diphenylphosphanyl)buta-1,3-dienes (**10**) via a *cis*-addition of the P-H bond to the C≡C triple bonds. Substituents such as methyl, phenyl, and trimethylsilyl are tolerated at the butadiyne. In a fast reaction, 1,4-bis(diphenylphosphanyl)-1,3-butadienes **10** (NUPHOS) were formed quantitatively via a catalytic cycle proposed in Figure 3.2.

Figure 3.2: Catalytic cycle of the hydrophosphanylation of butadiynes with diphenylphosphane in the presence of catalytic amounts of $[(thf)_4Ca(PPh_2)_2]$ (**8**) in THF solution (see text).



In solution dissociation of complex $[(thf)_4Ca(PPh_2)_2]$ and release of THF molecules leads to formation of a free coordination site. In the catalytic cycle shown in figure 3.2 the THF molecules are neglected. The Ca-P bond adds to one of the C≡C triple bonds yielding complex **A**. A similar addition reaction was observed earlier for the reaction of $[Mg\{P(SiMe_3)_2\}_2]$ [185] and $[Ca\{P(SiMe_3)_2\}_2]$ to diphenylbutadiyne, however, in this case the Ca derivative immediately undergoes a 1,3-trimethylsilyl shift yielding 2,5-diphenyl-3,4-bis(trimethylsilyl)phospholides [185]. Intermediate **A** contains a very reactive Ca-C σ-bond and immediately metallates $HPPh_2$ regaining the catalyst $Ca(PPh_2)_2$ and leading to the formation of intermediate 1,4-diphenyl-1-diphenylphosphanyl-1-butene-3-yne (**B**). Side-on coordination of alkynes to calcium [186] and barium cations [184] were observed earlier even in competition with THF molecules and therefore, the liberation of **B** could be slower than the addition of the Ca-P bond to the other C≡C triple bond yielding intermediate **C** with a Ca-C

bond. Again, metallation of another molecule of $HPPh_2$ leads to the catalyst **8** and the final product **10**. Now the catalytic cycle restarts again. The high yields of this hydrophosphination process shows that the vinylphosphanes are not able to undergo a further hydrophosphination reaction, even though calcium-mediated hydrophosphination of alkenes was reported for styrene and isoprene [134]. The above described cis addition represents the major reaction pathway. However, the intermediate organocalcium complex can also rearrange, yielding the cumulene intermediate **D**. Intermediate **D** also contains a very reactive Ca-C σ-bond and immediately reacts with $HPPh_2$ regaining the catalyst $Ca(PPh_2)$ and leading to the formation of intermediate **E.** Repetition of this reaction sequence yields the addition product **F** and finally butadiene **11**.

Table 3.2: Reaction conditions and yields of isolated diphenyl-vinylphosphanes obtained via hydrophosphanylation of alkynes and butadiynes in the presence of catalytic amounts of $[(thf)_4Ca(PPh_2)_2]$ **8** in THF solutions. For comparison reasons, selected examples from the literature are included.

Product	Employed alkyne	Solvent	Employed cat.	Mol% cat.	Yield[a)]	Ref.
9a	Ph-C≡C-Ph	THF	KO*t*Bu	10	26%	[181]
9a	Ph-C≡C-Ph	THF	$LiPPh_2/HNR_2$	[b)]	90%	[187]
9a	Ph-C≡C-Ph	THF	$[(thf)_4Ca(PPh_2)_2]$	6	77%	[136]
9a	Ph-C≡C-Ph	CH_3CN	$Pd(PPh_3)_4$	5	95%	[188a]
9a	Ph-C≡C-Ph	THF	Yb-catalyst[c)]	5	85%	[125a]
9a	Ph-C≡C-Ph	C_6D_6	Ca-catalyst[d)]	10	94%	[138]
9b	Ph-C≡C-Me	THF	Yb-catalyst[c)]	5	80%	[125a]
9b	Ph-C≡C-Me	THF	$[(thf)_4Ca(PPh_2)_2]$	5	85%	[136]
10a	Me-C≡C-C≡C-Me	THF	$[(thf)_4Ca(PPh_2)_2]$	5	81%	[137]
10b	Ph-C≡C-C≡C-Ph	THF	$[(thf)_4Ca(PPh_2)_2]$	5	89%	[137]
10c	Me_3Si-C≡C-C≡C-$SiMe_3$	THF	$[(thf)_4Ca(PPh_2)_2]$	5	79%	[137]
10d	Mes-C≡C-C≡C-Mes	THF	$[(thf)_4Ca(PPh_2)_2]$	5	76%	[137]

[a)] Yield of isolated vinylphosphanes regardless of *cis*- and *trans*-configuration. [b)] No values or details given in reference. [c)] Yb-catalyst$[(hmpa)_3Yb(\eta^2\text{-}Ph_2C{=}NPh)]$ was prepared prior to use without purification. [d)] Sterically encumbered $[\{HC(CMe{=}NAryl)_2\}Ca\{N(SiMe_3)_2\}(thf)]$ was used as calcium based catalyst.

Key values of the hydrophosphanylation of alkynes are summarized in Table 3.2. The yields refer to isolated crystalline colorless vinylphosphanes after work-up procedures. The calcium-mediated intermolecular hydrophosphanylation proceeded quantitatively within a few minutes as was shown by ^{31}P NMR spectroscopy. The C=C double bonds of the resulting vinylphosphanes are not hydrophosphanylated even in refluxing reaction mixtures.

Molecular Structures

The molecular structures of centrosymmetric 2,5-bis(diphenylphosphanyl)hexa-2,4-diene (**10a**), 1,4-diphenyl-1,4-bis(diphenylphosphanyl)buta-1,3-diene (**10b**), and 1,4-bis(trimethylsilyl)-1,4-bis(diphenylphosphanyl)buta-1,3-diene (**10c**) are shown in Figures 3.3 to 3.5. The compounds **10b** and **10c** originate from a twofold *cis*-addition of $HPPh_2$ to the C≡C triple bonds of the appropriate butadiyne giving the *trans*/*trans*-isomer. In contrast to theses derivatives hexadiene **10a** crystallizes as the *cis/cis*-isomer a result of a twofold *trans*-addition. The C1-C1A single bond and the C1=C2 double bond for the diphenylbutadiene **10b** show bond lengths of 143.9(9) and 135.1(6) pm, respectively, which hint toward a very week conjugation. The phenyl groups are oriented nearly perpendicular and are not communicating with the π-system of the butadiene backbone [C2-C15 149.0(6) pm]. The P-C bond lengths are equal within the standard deviations and show an average value of 183.0 pm which is characteristic for P-C single bonds. Similar bindings are valid for the other butadiyne systems. 1,4-Dimesityl-1,4-bis(diphenylphosphanyl)butadiene (**10d**) is displayed in figure 3.6 and contains no crystallographic symmetry elements. In contrast to **10b**, which crystallized as a *trans*/*trans*-isomer, this sterically more encumbered mesityl derivative precipitated as a *cis*/*cis*-isomer, the product of a twofold *trans*-addition of $HPPh_2$ to the alkyne units. The bulkiness of the substituents at the butadiene backbone play a dominating role in this isomerism. The Ca-C bonds are mainly ionic and therefore, the following equilibrium seems to be fast in comparison to the addition step:

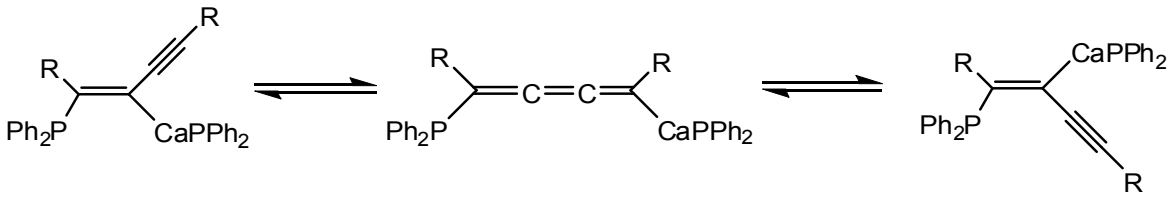


Figure 3.3: Molecular structure and numbering scheme of 2,5-bis(diphenylphosphanyl)hexa-2,4-diene (**10a**). The ellipsoids represent a probability of 40%, H atoms are neglected for clarity reasons. Symmetry-related atoms (-x, -y+1, -z) are marked with an "A". Selected structural data are listed in Table 3.

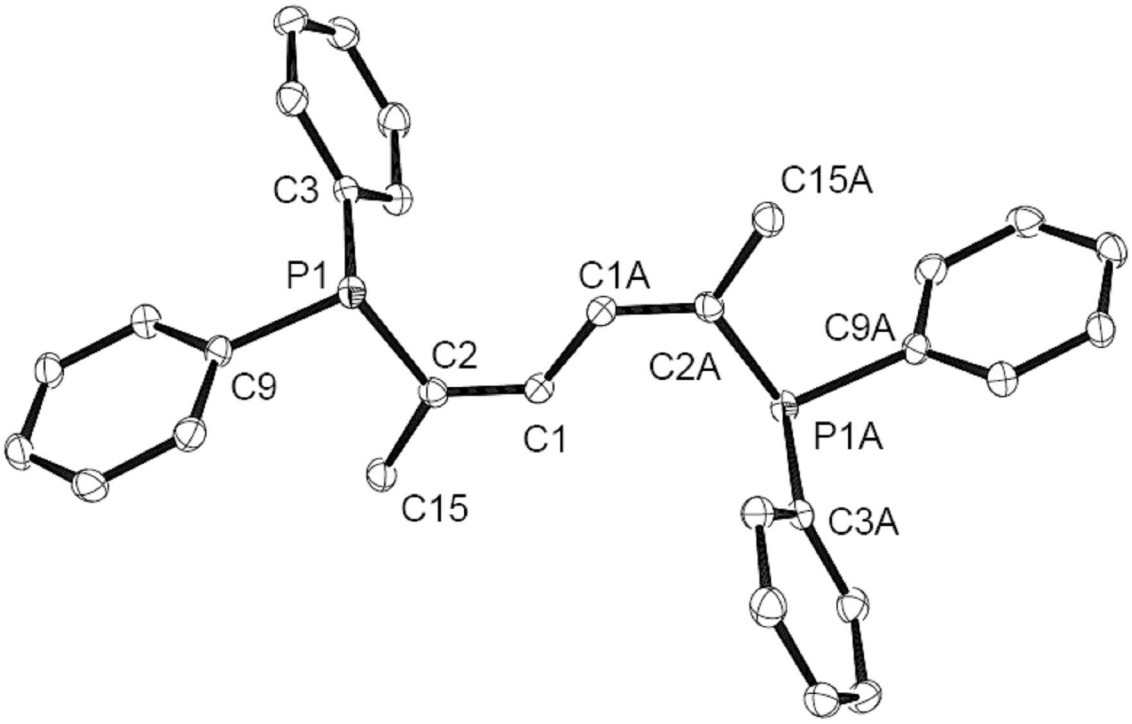


Figure 3.4: Molecular structure and numbering scheme of 1,4-diphenyl-1,4-bis(diphenylphosphanyl)buta-1,3-diene (**10b**). The ellipsoids represent a probability of 40%, H atoms are omitted for clarity reasons. Symmetry-related atoms (-x, -y+1, -z) are marked with an "A". Selected structural data are listed in Table 3.

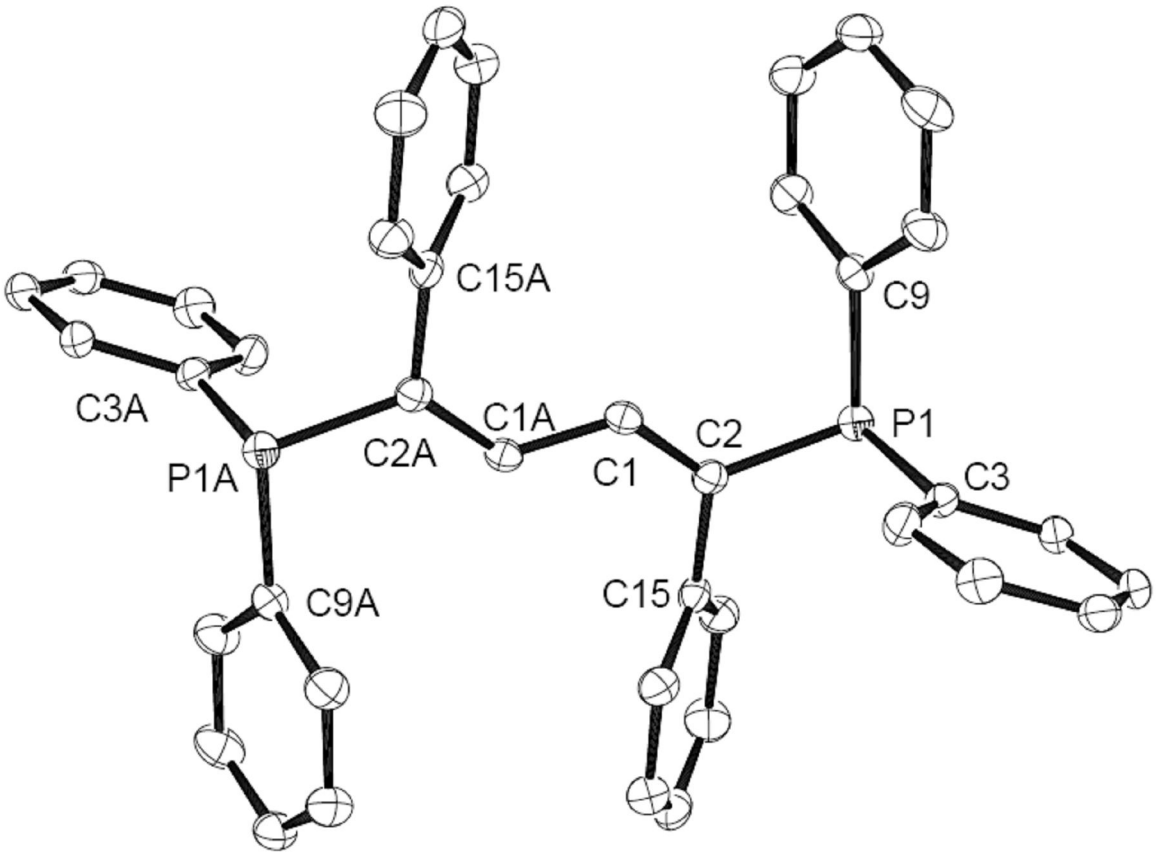


Figure 3.5: Molecular structure and numbering scheme of 1,4-bis(trimethylsilyl)-1,4-bis(diphenylphosphanyl)buta-1,3-diene (**10c**). The ellipsoids represent a probability of 40%, H atoms are not drawn. Symmetry-related atoms (-x+1, -y, -z+1) are marked with an "A". Selected structural data are listed in Table 3.

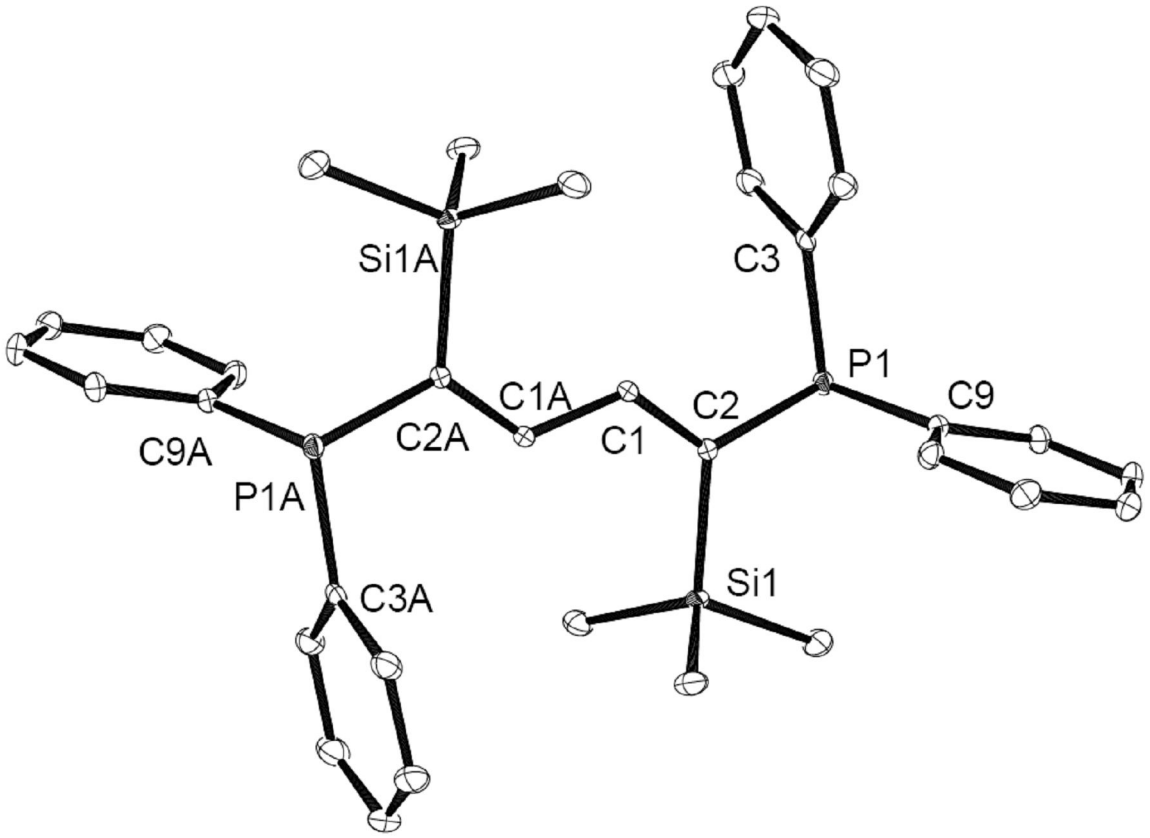


Figure 3.6: Molecular structure and numbering scheme of 1,4-dimesityl-1,4-bis(diphenylphosphanyl)buta-1,3-diene (**10d**). The ellipsoids represent a probability of 40%, H atoms are not shown for clarity reasons. Selected bond lengths (pm): P1-C1 183.3(2), P1-C23 182.6(2), P1-C29 183.3(2), P2-C4 186.1(2), P2-C35 184.0(2), P2-C41 182.9(2), C1-C2 134.5(3), C2-C3 146.5(3), C1-C5 150.4(3), C3-C4 134.5(3), C4-C14 150.3(3). Bond angles (°): C1-P1-C23 103.55(9), C1-P1-C29 103.54(9), C23-P1-C29 101.55(10), C4-P2-C35 103.66(9), C4-P2-C41 102.40(9), C35-P2-C41 101.56(10), C1-C2-C3 126.69(19), C2-C1-C5 119.02(17), C2-C1-P1 119.82(14), C5-C1-P1 120.94(14). C3-C4-P2 119.25(14), C14-C4-P2 121.42(14).

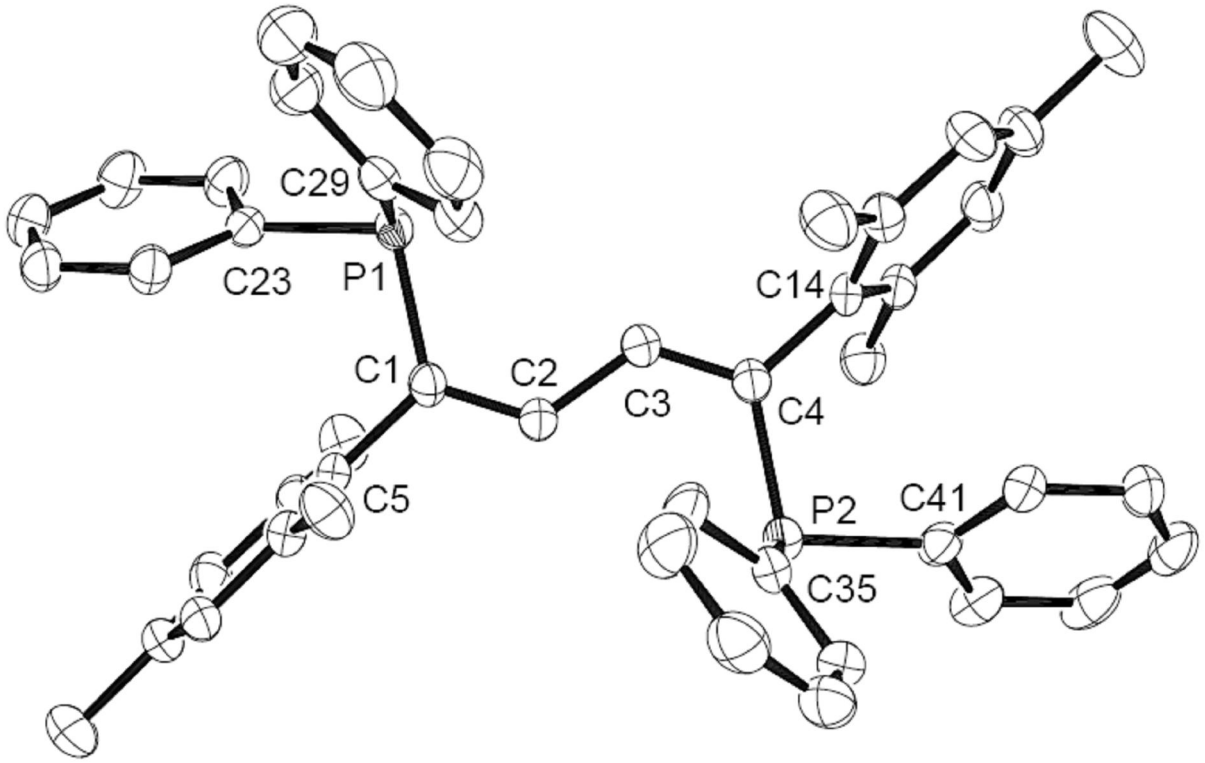
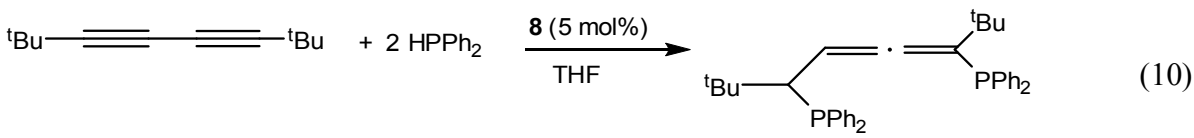


Table 3.3: Comparison of selected structural data of the NUPHOS diphosphanes $Ph_2P(R)C{=}CH{-}CH{=}C(R)PPh_2$ **10a** (R = Me), **10b** (R = Ph), **10c** (R = $SiMe_3$) and **10d** (R = Mes).

	10a (R = Me)	**10b** (R = Ph)	**10c** (R = $SiMe_3$)	**10d** (R = Mes)[a]
C1-C1A	144.0(4)	143.9(9)	145.7(4)	146.5(3)
C1-C2	135.0(3)	135.1(6)	135.3(3)	134.5(3)
C2-P1	184.3(2)	183.0(5)	182.6(2)	185.3(2)
C2-Si1/C	150.0(3)	149.0(6)	189.8(2)	150.4(3)
P1-C3	184.0(2)	182.6(5)	183.0(2)	182.6(2)
P1-C9	183.9(2)	183.3(5)	183.1(2)	183.3(2)
C1A-C1-C2	126.6(3)	126.3(5)	125.4(2)	126.69(19)
C1-C2-P1	119.5(2)	124.5(4)	121.0(1)	119.82(14)
C1-C2-Si1/C	121.1(2)	123.1(4)	123.3(1)	119.09(17)
P1-C2-Si1/C	119.4(2)	112.4(3)	115.4(1)	119.55(14)
C2-P1-C3	101.88(9)	101.2(2)	103.86(8)	103.55(9)
C2-P1-C9	101.22(9)	105.0(2)	101.98(9)	103.54(9)
C3-P1-C9	101.94(9)	102.4(2)	103.97(9)	101.55(10)

a) Average values.

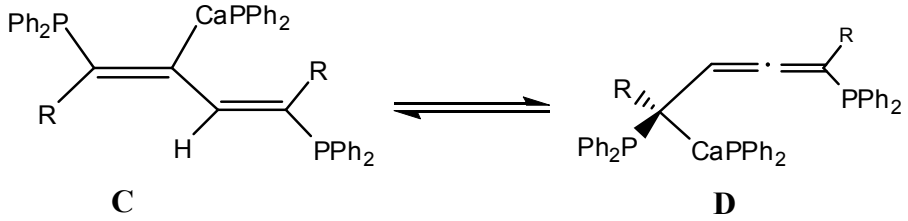
The behavior of di-tert-butylbuta-diyne (2,2,7,7-tetramethylocta-3,5-diyne) seems to be very different from that of the other diynes. Thus, its reaction with **8** at -78 °C gave bis(diphenylphosphanyl)allene **12** with a yield of 70% according to equation 10.



(10)

A similar addition reaction was observed earlier. The use of $Yb(\eta^2\text{-}Ph_2CNPh)(hmpa)_3$ [127] and $Yb[N(SiMe_3)_2]_3(hmpa)_2$ as catalysts in the reaction of di-tert-butylbutadiyne with $HPPh_2$ at -35 °C for 2 hours gave an allene and (Z,Z)-diene with yields of 71% and 12%, respectively. If the reaction was performed at room temperature in the presence of these catalysts, exclusively the allene was obtained in high yields [127], after oxidation with H_2O_2. The addition of $HPPh_2$ to di(tert-butyl)butadiyne in the presence of catalytic amounts of

[(thf)$_4$Ca(PPh$_2$)$_2$] yields allene **12** according to equation 10. This reaction product can be explained via the equilibrium shown in scheme 1, a 1,3-shift of the CaPPh$_2$ moiety.



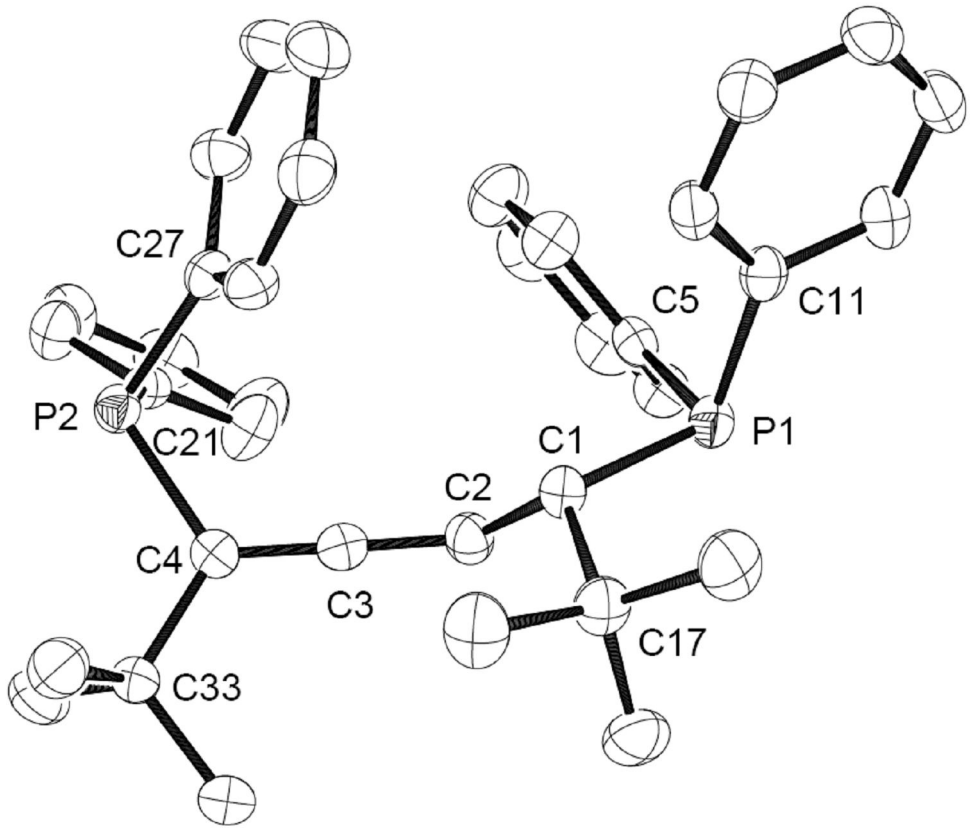
C **D**

Scheme 1:

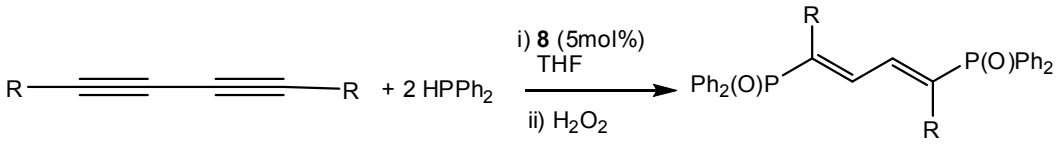
Formation of the allene **12** from the di-tert-butylbutadiene intermediate. In this case, two tertiary substituents caused severe steric crowding in the form of a dienylcalcium species, and thus the allenic **D** should be the most stable intermediate to give **12**.

The molecular structure of 3,6-bis(diphenylphosphanyl)-2,2,7,7-tetramethyl-3,4-octadiene (**12**) is shown in Figure 3.7. The C2-C3 and C3-C4 double bonds show bond lengths of 130.3(3) and 130.7(3) pm, respectively, which are characteristic for a cumulene system. These values are smaller than to the values of the double bonds of diphenyl, dialkyl, and trialkylsilyl butadiene systems. This observation can be addressed to the larger s-orbital contribution because the middle C3 atom is sp-hybridized. The C2-C3-C4 bond angle is 177.3° and shows only a small deviation from linearity.

Figure 3.7: Molecular structure and numbering scheme of 3,6-bis(diphenylphosphanyl)-2,2,7,7-tetramethyl-3,4-octadiene (**12**). The ellipsoids represent a probability of 40%, H atoms are omitted for clarity reasons. Selected bond lengths (pm): P1-C1 188.0(2), P1-C5 183.2(2), P1-C15 184.2(2), P2-C4 185.0(2), P2-C21 183.3(2), P2-C27 183.2(2), C1-C2 151.2(3), C1-C17 156.1(3), C2-C3 130.3(3), C3-C4 130.7(3), C4-C33 154.0(3). Bond angles (°): C1-P1-C11 105.04(10), C1-P1-C5 101.88(10), C5-P1-C11 99.73(10), C1-C2-C3 127.4(2), C2-C1-C17 113.41(17), C2-C3-C4 177.3(2), C3-C4-C33 123.4(2), C2-C1-P1 107.95(15), C17-C1-P1 111.99(15), C3-C4-P2 120.99(17), C33-C4-P2 115.54(15).



We next investigated the scope of the hydrophosphanylation of butadiyenes with a subsequent oxidation. Treatment of the butadiyne system with 2 equiv. of $HPPh_2$ in the presence of **8** (5 mol%) in THF at -78 ºC for one hour, and oxidation with H_2O_2 afforded the phosphane oxides **13a, 13b, 13c** (equation 11). The products showed one resonance each at 36.1 ppm, 33.6 ppm, and 40.8 ppm, respectively, in the ^{31}P NMR spectra. Crystallization led to the precipitation of the (E,E)-isomers, which were the major products. In a similar procedure Kimihiro performed a catalytic hydrophosphanylation of 1,4-diphenylbutadiyne exclusively obtained polymers using $Yb(\eta^2\text{-}Ph_2CNPh)(hmpa)_3$ as a catalyst; with catalytic amounts of $Yb[N(SiMe_3)_2]_3(hmpa)_2$ the isolation of the (E,E)-isomer succeeded with low yields [127].



(11)

R = Me (**13a**), Ph (**13b**), $SiMe_3$ (**13c**)

Molecular Structures

The molecular structures of 2,5-bis(diphenylphosphanyl)hexa-2,4-diene (**13a**), 1,4-bis(diphenylphosphanyl)-1,4-diphenyl-buta-1,3-diene (**13b)** and 1,4-bis(diphenylphosphanyl)-1,4-Bis(trimethylsilyl)-buta-1,3-diene (**13c**) are shown in Figures 3.8-3.10. All compounds crystallized as trans/trans isomers. The C2-C2A/C3 single bonds and the C1=C2 double bonds for the hexadiene derivative **13a**, diphenylbutadiene **13b** and trimethylsilyl butadiene **13c** show bond lengths of 145.9(5) and 133.8(4) pm, 145.7(3) and 134.9(3) pm, 146.1(4) and 135.0(2) pm, respectively. The C=C bond length in these molecules is within the same range as reported for other C=C containing compounds. The C-C single bond in **13** is slightly shorter than a normal C-C single bond (154 pm), this might be due to multiple bond character obtained by delocalization [188b]. The P-O bond lengths of **13a**, **13b** and **13c** are 148.6(2) pm, 148.9(2) pm and 148.6(1) pm, respectively, being very similar to those found from spectroscopic studies of the free P-O bond (147.0 pm) [188c] and similar to the P-O bond (148.0 pm [188d] and 147.9 pm [188e]) of $OPPh_3$. The P-C bond lengths are all equivalent within the standard deviations and show average values of 180.5 pm for **13a**, 180.3 pm for **13b** and 180.9 pm for **13c**, respectively. They are characteristic for P-C single bonds. These average values are significantly shorter than P-C bonds in **10a** with 184.0 pm, **10b** with 183.0 pm [136] and **10c** with 183.0 pm. This shortening could be the consequence of the electron-

withdrawing properties of the phosphoryl oxygen atom and of the larger oxidation state. Due to the larger demand of the P=O double bond, the O-P-C bond angles, average values of 113.0° for **13a**, 112.0° for **13b** and 111.9° for **13c**, respectively, are larger than the tetrahedral angle of 109.5°, while the C-P-C bond angles, (average values: 106.0° for **13a**, 106.6° for **13b** and 106.7° for **13c**) are smaller than the tetrahedral angle. The phenyl groups in **13b** are oriented nearly perpendicular to the butadiene backbone and are not communicating with the butadiene π-system [C1-C5 148.9(3), C4-C11 148.5(3)].

Figure 3.8: Molecular structure of 2,5-bis(diphenylphosphanyl)hexa-2,4-diene (**13a**). The ellipsoids represent a probability of 40%, H atoms are omitted for clarity reasons. Symmetry-related atoms (-x, -y, -z) are marked with an "A". Selected bond lengths (pm): P1-C1 180.7(3), P1-C4 180.3(3), P1-C10 180.4(3), P1-O1 148.6(2), C1-C2 133.8(4), C1-C3 149.9(4), C2-C2A 145.9(5). Bond angles (°): C1-P1-C4 106.57(12), C1-P1-C10 105.93(12), C1-P1-O1 112.98(12), C2A-C2-C1 125.0(3), C2-C1-C3 125.6(2), C2-C1-P1 116.2(2), and C3-C1-P1 118.15 (19).

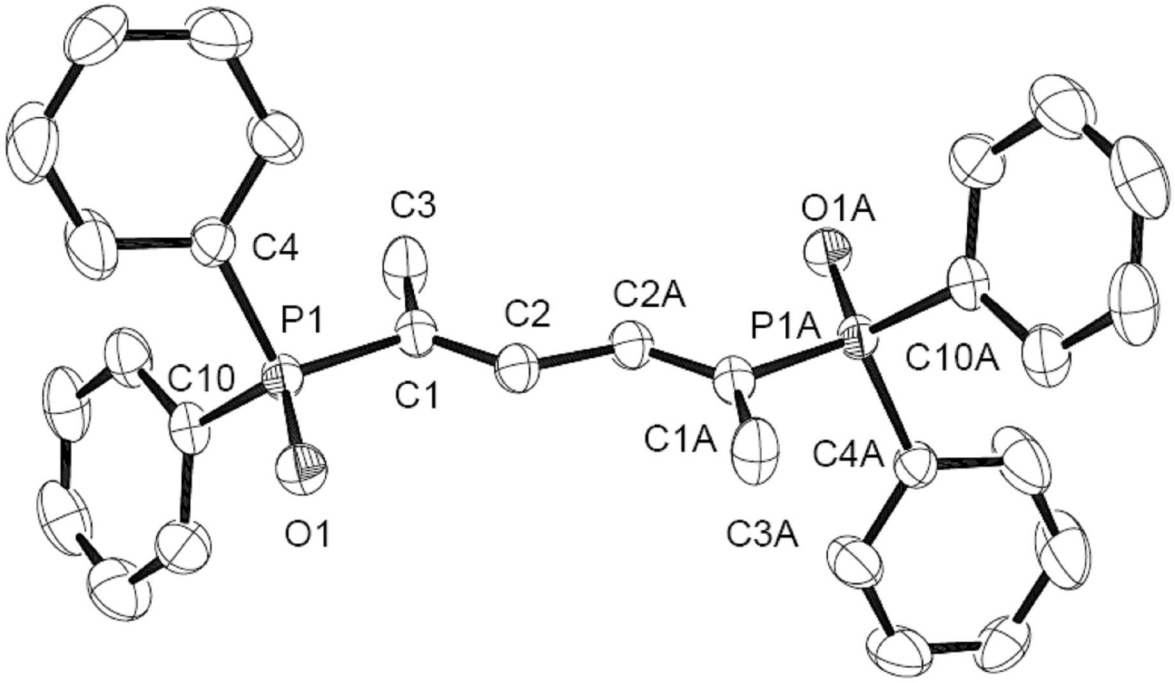


Figure 3.9: Molecular structure of 1,4-bis(diphenylphosphanyl)-1,4-diphenyl-buta-1,3-diene (**13b**). The ellipsoids represent a probability of 40%, H atoms are neglected. Selected bond lengths (pm): P1-C1 180.7(2), P1-C17 179.8(3), P1-C23 179.1(2), P1-O1 148.89(16), P2-C4 180.5(2), P2-C29 181.0(3), P2-C35 179.4(2), P2-O2 148.34(19),C1-C2 134.9(3), C1-C5 148.9(3), C2-C3 145.7(3), C3-C4 134.3(3), C4-C11 148.5(3). Bond angles (°): C1-P1-C17 106.02(11), C1-P1-C23 106.85(11), C1-P1-O1 111.99(10), C2-C3-C4 125.6(2), C3-C4-C11 122.9(2), C3-C4-P2 119.10(18), C11-C4-P2 118.03(16), C3-C2-C1 123.3(2), C2-C1-C5 120.6(2), C2-C1-P1 121.09(18), C5-C1-P1 118.34(16).

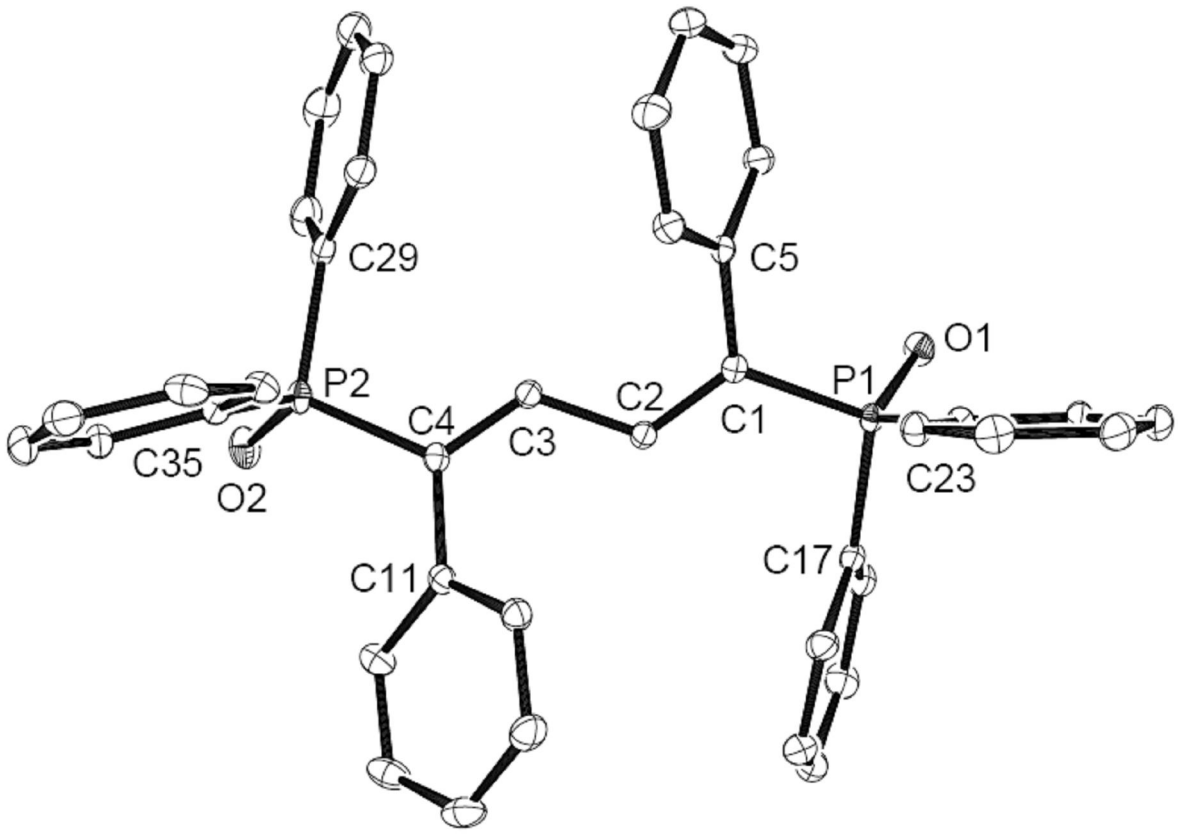


Figure 3.10: Molecular structure of 1,4-Bis(diphenylphosphinyl)-1,4-Bis(trimethylsilyl)-buta-1,3-diene (**13c**). The ellipsoids represent a probability of 40%, H atoms are omitted for clarity reasons. Symmetry-related atoms (-x, -y, -z) are marked with an "A". Selected bond lengths (pm): P1-C1 181.14(18), P1-C6 181.01(19), P1-C12 180.60(19), P1-O1 148.58(14), C1-C2 135.0(2), C1-Si1 191.04(19), C2-C2A 146.1(4). Bond angles (°): C1-P1-C6 108.43(8), C1-P1-C12 105.75(8), C1-P1-O1 112.38(8), C12-P1-C6 105.85(9), C2A-C2-C1 125.7(2), C2-C1-Si1 124.22(14), C2-C1-P1 117.16(14), Si1-C1-P1 118.39(9).

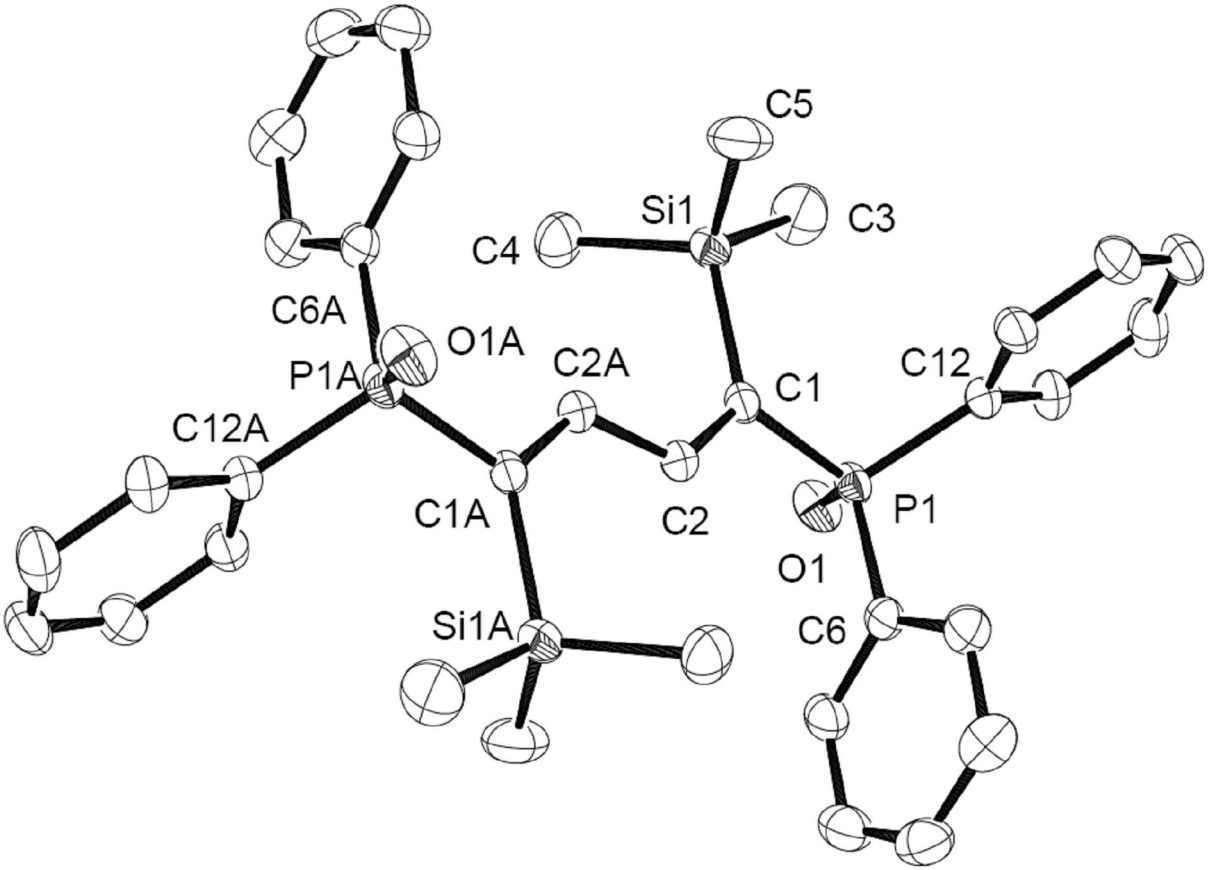


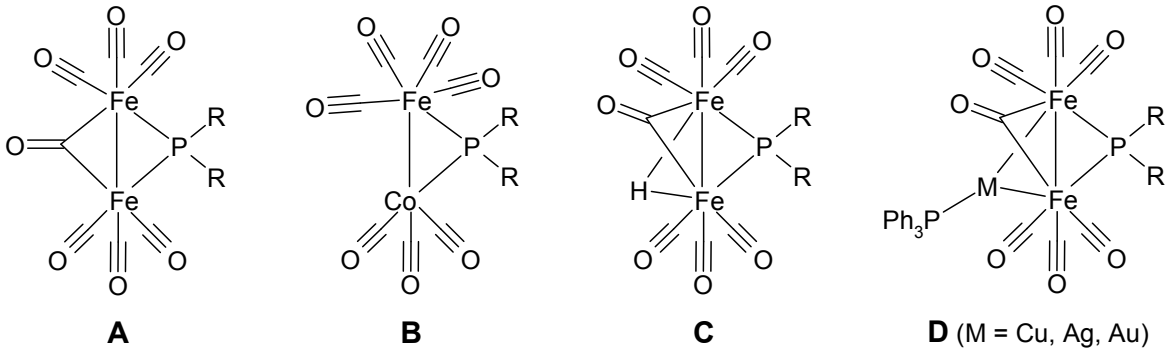
Table 3.4: Comparison of selected structural parameters of the compounds $\{Ph_2P(O)\}C(R)=CH-CH=C(R)\{P(O)Ph_2\}$ **13a** (R = Me), **13b** (R = Ph) and **13c** (R = $SiMe_3$) (average values).

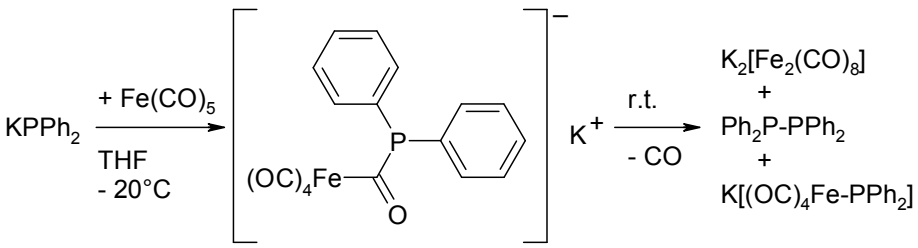
	5a (R = Me)	**5b** (R = Ph)	**5c** (R = $SiMe_3$)
C-C	145.9(5)	145.7(3)	146.1(4)
C=C	133.8(4)	134.9(3)	135.0(2)
P=O	148.6(2)	148.89(16)	148.58(14)
P-C_{Ph}	180.3(3)	179.8(3)	180.60(19)
P1-C_{vi}	180.7(3)	180.7(2)	181.14(18)
P-C1-C2	116.2(2)	121.09(18)	117.16(14)
O1-P1-C1	112.98(12)	111.99(10)	112.38(8)
O1-P1-C4	112.93(12)	112.10(11)	111.37(9)
O1-P1-C10	112.11(12)	112.46(11)	112.67(8)
C1-P1-C4	106.57(12)	106.02(11)	108.43(8)
C1-P1-C10	105.75(13)	106.85(11)	105.75(8)
C4-P1-C10	105.75(13)	107.00(11)	105.85(9)

3.3. Synthesis and X-Ray Crystal Structure of $[(thf)_4Ca\{Fe_2(CO)_6(\mu\text{-}CO)(\mu\text{-}PPh_2)\}_2]$.

We are interested in the reaction behaviour of easily accessible $[(thf)_4Ca(PPh_2)_2]$ [18,19]. This complex shows an enormous reactivity as a catalyst in hydrophosphanylation reactions [136]. The coordination behaviour of the nucleophilic phosphanide anion offers various possibilities in coordination chemistry.

Petz and Weller [189] investigated the reaction of $KPPh_2$ with $Fe(CO)_5$ in THF at -20°C. The first reaction step consisted of an addition of the PPh_2 nucleophile to a carbonyl group leading to the formation of $K[(OC)_4Fe\text{-}C(O)\text{-}PPh_2]$ with a chemical shift of $\delta(^{31}P)$ = 46.4 ppm and a C=O stretching frequency of 1670 cm^{-1} for the keto group. However, this compound decomposed at room temperature *via* a radical mechanism yielding $[Fe(CO)_8]^{2-}$, $Ph_2P\text{-}PPh_2$ $\{\delta(^{31}P)$ = -14.4 ppm$\}$, and $K[(OC)_4Fe\text{-}PPh_2]$ $\{\delta(^{31}P)$ = -2.4 ppm$\}$ as is shown in equation 12. In addition, it was reported that complexes with the anion $[\{(OC)_4Fe\}_2PPh_2]^-$ (**E**$^-$) (which shows a ^{31}P NMR resonance at a position of approximately 75 ppm to higher field than **A**$^-$) decarbonylate readily yielding quantitatively the heptacarbonyl anion $[Fe_2(CO)_6(\mu\text{-}CO)(\mu\text{-}PPh_2)]^-$ (**A**$^-$) [190,191] with a ^{31}P NMR shift of approximately $\delta(^{31}P)$ = 125 ppm [140].

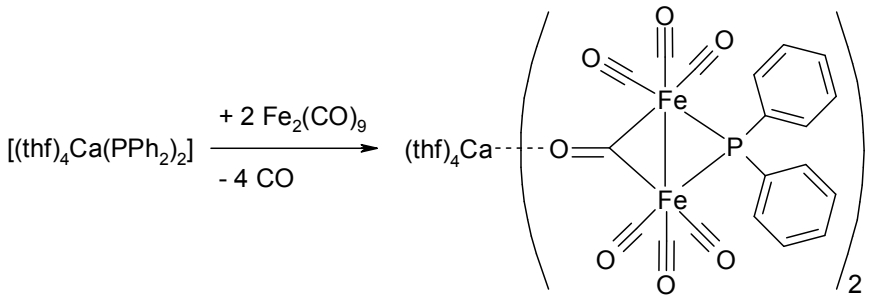




(12)

We investigated and reported a new access route to $[(thf)_4Ca\{Fe_2(CO)_6(\mu\text{-}CO)(\mu\text{-}PPh_2)\}_2]$ (**14**) with a yet unknown coordination behaviour of the anion *via* the oxygen atom of the bridging carbonyl ligand [192].

The reaction of $[(thf)_4Ca(PPh_2)_2]$ with excess of iron carbonyls $Fe(CO)_5$, $Fe_2(CO)_9$, or $Fe_3(CO)_{12}$ proceeded stepwise, finally leading to the formation of $[(thf)_4Ca\{Fe_2(CO)_6(\mu\text{-}CO)(\mu\text{-}PPh_2)\}_2]$ (**14**). The ^{31}P NMR spectroscopic pursuit of these reactions showed at the beginning resonances at $\delta(^{31}P)$ = 43 ppm and at $\delta(^{31}P)$ = 61 ppm with varying intensity ratios besides the resonance at $\delta(^{31}P)$ = -13 ppm of the compound $[(thf)_4Ca(PPh_2)_2]$. In Figure 3.11 the $^{31}P\{^1H\}$ NMR spectra at the beginning of the reaction and after heating for few hours are shown. Removal of the solvent or prolonged heating of the reaction mixtures led to extensive conversion of the intermediates at $\delta(^{31}P)$ = 43 ppm and $\delta(^{31}P)$ = 61 ppm to **14** at $\delta(^{31}P)$ = 128 ppm. Our observations can be explained in terms of simultaneous formation of $[(OC)_4Fe\text{-}C(O)\text{-}PPh_2]^-$ and $[\{(OC)_4Fe\}_2PPh_2]^-$ (**E**$^-$) in analogy to published investigations [127,134,189]. Prolonged heating of these reaction mixtures led to liberation of carbon monoxide which drives the reaction toward the formation of the orange-red contact ion pair $[(thf)_4Ca\{Fe_2(CO)_6(\mu\text{-}CO)(\mu\text{-}PPh_2)\}_2]$ (**14**) which showed a six-coordinate calcium atom in the solid state and the carbonylferrate units in a trans position (equation 13). Compound **14** was only slightly air sensitive but hygroscopic.



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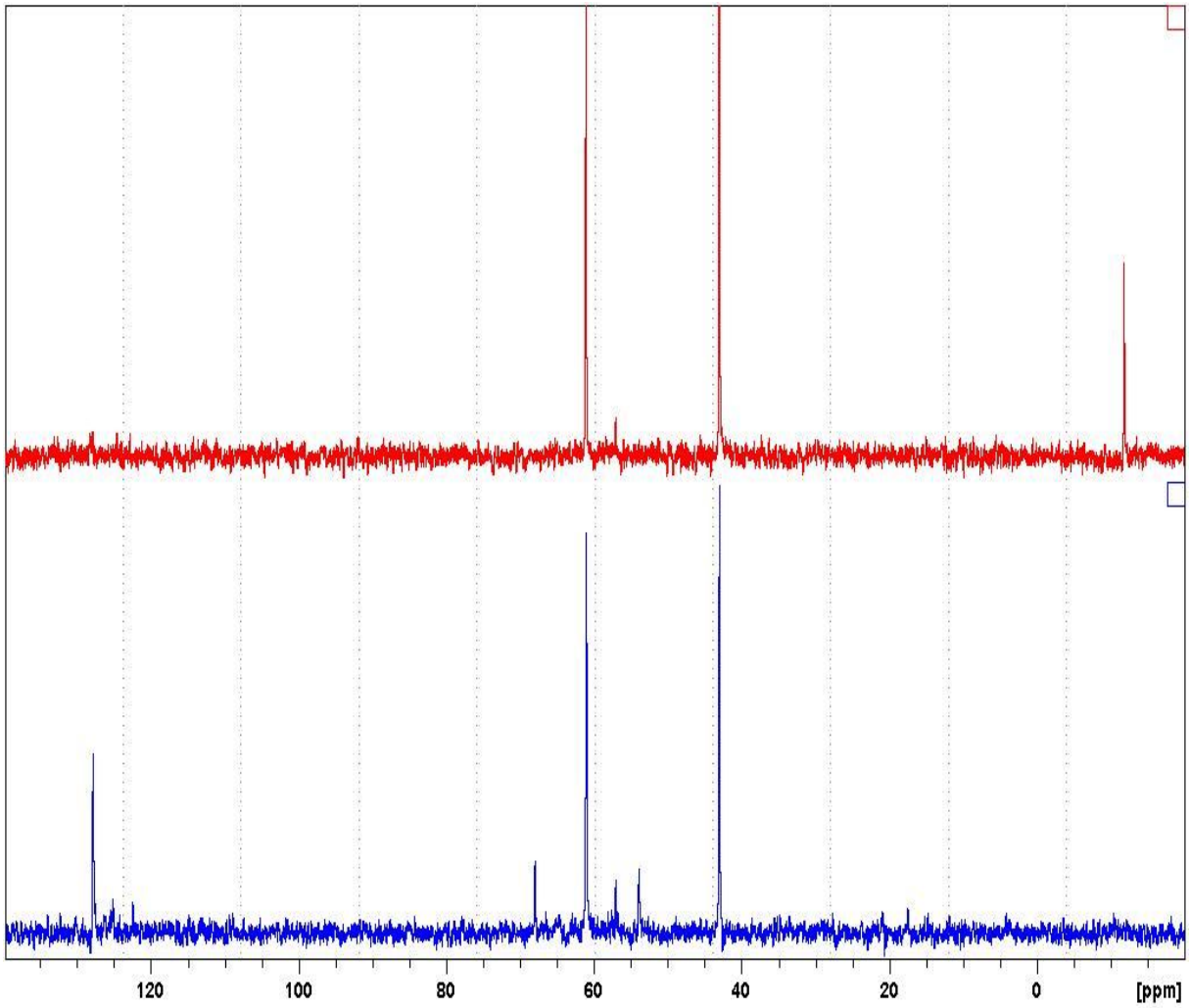
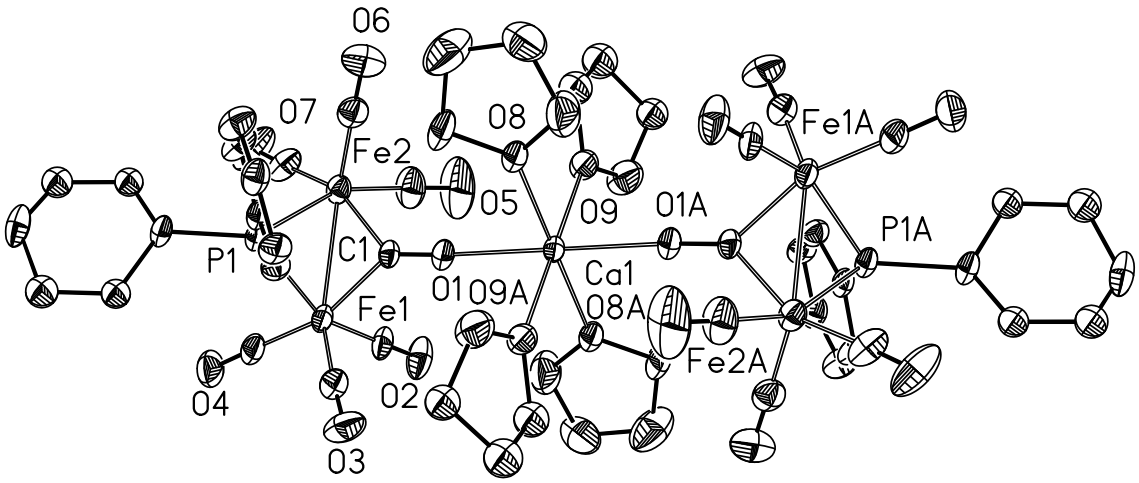


Figure 3.11: The $^{31}P\{^{1}H\}$ NMR spectrum of the reaction product of $[(thf)_4Ca(PPh_2)_2]$ [$\delta(^{31}P)$ = -13 ppm] with $Fe_3(CO)_{12}$ in THF immediately after addition (upper spectrum) and after 4 hours of heating under reflux (lower spectrum) (81.014 MHz, $[D_8]$THF).

Molecular structure of 14

Molecular structure and numbering scheme of **14** are shown in Figure 3.12. The calcium center shows a distorted octahedral environment with rather short Ca-O distances of 229.8 and 234.0 pm (average values) to the bridging carbonyl and to the THF molecules, respectively. The smaller value is partly a consequence of lower steric strain around the oxygen atom of the carbonyl group.

Figure 3.12: Molecular structure and numbering scheme of $[(thf)_4Ca\{Fe_2(CO)_6(\mu\text{-}CO)(\mu\text{-}PPh_2)\}_2]$ (**14**). The ellipsoids represent a probability of 40%, H atoms are neglected for clarity reasons. Symmetry related atoms (-x+2, -y+2, -z) are marked with the letter "A". Selected bond lengths (pm): Ca1-O1 229.8(4), Ca1-O8 233.5(4), Ca1-O9 234.5(4), Fe1-Fe2 257.9(2), Fe1-C1 192.7(6), Fe1-C2 176.4(6), Fe1-C3 176.4(7), Fe1-C4 180.8(7), Fe1-P1 221.9(2), Fe2-C1 192.2(6), Fe2-C5 176.4(7), Fe2-C6 176.1(8), Fe2-C7 179.8(7), Fe2-P1 222.5(2), C1-O1 122.1(6), C2-O2 115.9(7), C3-O3 115.4(7), C4-O4 115.5(7), C5-O5 114.6(8), C6-O6 114.9(8), C7-O7 114.5(7).



Selected structural parameters of the $[Fe_2(CO)_6(\mu\text{-}CO)(\mu\text{-}PR_2)]^-$ anions ($\mathbf{A}^-$) are summarized in Table 3.5. In order to compare the Fe-P distances the influence of the P-bound groups has to be considered. In $[Fe_2(CO)_6(\mu\text{-}PPh_2)(\mu\text{-}P\textit{t}Bu_2)]$ all carbonyl ligands are terminally coordinated and both phosphanide anions occupy bridging positions [193]. The dialkyl substituted phosphanide shows a larger average Fe-P distance of 227.0 pm than the Fe(μ-PPh_2) moiety (av. 225.5 pm). In the structure of $[Fe_2(CO)_5(NO)(PPh_3)(\mu\text{-}P\textit{t}Bu_2)]$ [194] the Fe-P bond lengths to terminally bound PPh_3 and to bridging $P\textit{t}Bu_2$ are very similar suggesting that the coordination number of the phosphorus atom is the major influence on the Fe-P bond lengths. In the anion $[(OC)_4Fe\text{-}PPh_2]^-$ repulsive forces between the phosphanide anion and the rather electron-rich iron center lead to large Fe-P distances of 235.9 pm despite the low

coordination number of three for the P atom [189]. The rather weak interaction between iron and phosphorus in this solvent-separated ion pair allows short Fe-C bonds to the carbonyl ligands. The coordination of another $Fe(CO)_4$ moiety and the formation of $[\{(OC)_4Fe\}_2PPh_2]^-$ leads to a shortening of the Fe-P bonds despite the enhancement of the coordination number of the phosphorus atom and an enlargement of the Fe-C distances [139].

Table 3.5: Selected structural parameters (average values) for iron carbonyl complexes with additional phosphanide substituents. For comparison purposes, $[(OC)_4Fe\text{-}PPh_3]$ and $[FeCo(CO)_7(\mu\text{-}PR_2)]$ are included.

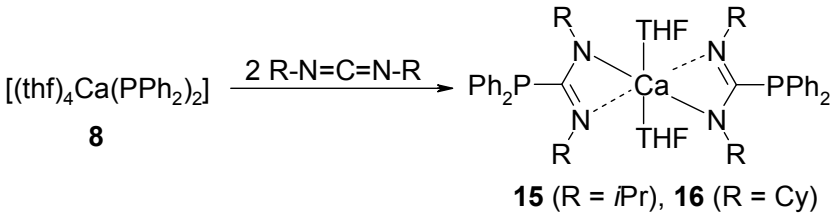
Compound[a]	Fe-P	Fe-Fe	Fe-C_t	Fe-C_b	Ref.
$[(OC)_4Fe\text{-}PPh_3]$	224.4	-	179.5	-	[195]
$[(OC)_4Fe\text{-}PPh_2(CH_2)_2PPh_2]$	224.6	-	178.6	-	[196]
$[K(18C6)][(OC)_4Fe\text{-}PPh_2]$	235.9	-	175.6	-	[189]
$[Fe_2(CO)_6(NO)(\mu\text{-}PPh_2)]$	222.6	269.9	179.9	-	[197]
$[FeCo(CO)_7(\mu\text{-}PMe_2)]$	222.8	266.6[b]	181	-	[143]
$[\{(OC)_4Fe\}_2PPh_2]^-$ [c]	232.5	-	176.2	-	[139]
$[(thf)_4Ca\{Fe_2(CO)_6(\mu\text{-}CO)(\mu\text{-}PPh_2)\}_2]$ (**14**)	222.2	257.9	177.7	192.5	[192]
$[NEt_4][Fe_2(CO)_6(\mu\text{-}CO)(\mu\text{-}PPh_2)]$	221.0	260.1	177.8	196.4	[142]
$[(Ph_3P)_2N][Fe_2(CO)_6(\mu\text{-}CO)(\mu\text{-}P\textit{t}Bu_2)]$	224.9	262.7	177.1	196.4	[144]
$[Fe_2(CO)_6(\mu\text{-}CO)(\mu\text{-}H)(\mu\text{-}P\textit{t}Bu_2)]$	227.4	260.3	180.6	197.7	[144]
$[Fe_2(CO)_6(\mu\text{-}CO)(\mu\text{-}PPh_2)\{\mu\text{-}Cu(PPh_3)\}]$	222.8	262.7	178.2	197.3	[145]
$[Fe_2(CO)_6(\mu\text{-}CO)(\mu\text{-}P\textit{t}Bu_2)\{\mu\text{-}Ag(PPh_3)\}]$	227.3	265.6	178.3	196.4	[140]

[a] Methyl, Me; phenyl, Ph; *tert*-butyl, ^{t}Bu; 18-crown-6, 18C6. [b] Fe-Co bond length. [c] Counter cation: $[Fe_2(CO)_5(PMe_3)_3(\mu\text{-}PPh_2)]^+$.

The C-O bond lengths strongly depend on the coordination mode. The C1-O1 bond of the bridging carbonyl ligand is elongated compared to the bond lengths in terminally bound carbonyl groups. This fact is in agreement with the expectation that bridging carbonyl groups should exhibit a C=O bond order of two (comparable to ketones), whereas terminally bound carbonyl groups should show a higher bond order (comparable to the isoelectronic cyanide). Within the group of terminally bound carbonyl ligands, significant differences can be noticed. The Fe1-C4 and Fe2-C7 bonds in trans-position to the bridging carbonyl goup C1-O1 show significantly larger Fe-C distances due to the trans influence of the bridging carbonyl ligand.

3.4. [Bis(tetrahydrofuran-*O*)-bis(1,3-dialkyl-2-diphenylphosphanyl-1,3-diazaallyl)calcium] – Synthesis and Crystal Structures of Catalytically Active Calcium Bis[phospha(III)guanidinates]

Starting $[(thf)_4Ca(PPh_2)_2]$ (**8**) is easily accessible via the metathesis reaction of $KPPh_2$ with anhydrous CaI_2 in THF [18,19] and to dialkylcarbodiimides RN=C=NR [R = isopropyl (*i*Pr), cyclohexyl (Cy)] readily add to this calcium complex according to equation 14 [148]. In another procedure the potassium salt $KPPh_2$ can be reacted with carbodiimides and the subsequent metathesis reaction with anhydrous calcium (II) iodide also yields the phospha(III)guanidinate complexes **15** and **16** [148]. Yields above 70% were achieved, however, depending on the reaction conditions varying amounts of the protonated phospha(III)guanidines were also observed in the reaction mixtures due to the reaction of **15** and **16** with still present $HPPh_2$ [148] (Fig 3.13, see below).



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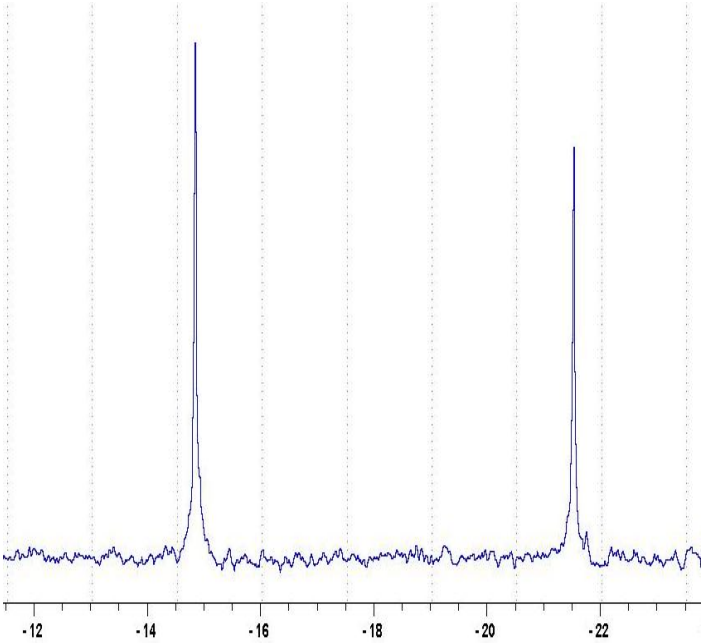


Figure 3.13: $^{31}P\{^1H\}$ NMR spectrum of the reaction mixture of $[(thf)_4Ca(PPh_2)_2]$ (**8**) with Cy-N=C=N-Cy in THF. The resonances at δ = -21.5 and -14.9 correspond to the calcium complex

16 and its protonation product Ph_2P-C(=NCy)N(H)Cy, respectively (81.014 MHz, THF, 25°C).

Molecular structures and numbering schemes of **15** and **16** are shown in Figures 3.14 and 3.15, respectively. In both complexes the calcium atoms are in distorted octahedral environments and the phospha(III)guanidinate ligands act as bidentate ligands *via* the nitrogen donors. However, in the *N,N'*-diisopropyl substituted derivative **15** the THF molecules show a *cis* coordination whereas in the *N,N'*-dicyclohexyl complex **16** a *trans* arrangement is realized. A *cis* arrangement similar as observed for **15** was reported earlier for $[(thf)_2Ca\{i\text{PrNC(NH}i\text{Pr)NPh}\}_2]$ [198] whereas the *trans* isomer shows similarities to the benzamidinates of calcium [199].

Figure 3.14: Molecular structure and numbering scheme of $[(thf)_2Ca\{i\text{PrNC}(PPh_2)N i\text{Pr}\}_2]$ (**15**). The ellipsoids represent a probability of 40%, hydrogen atoms are neglected for clarity reasons. Selected bond lengths (pm): Ca1-N1 242.1(2), Ca1-N2 243.2(2), Ca1-N3 243.9(2), Ca1-N4 240.8(2), Ca1-O1 242.6(2), Ca1-O2 242.5(2), C1-P1 191.0(2), C1-N1 132.1(3), C1-N2 133.3(3), N1-C2 146.0(3), N2-C5 145.4(3), C20-P2 190.1(2), C20-N3 134.1(3), C20-N4 132.5(3), N3-C21 146.4(3), N4-C24 146.0(3), P1-C8 183.4(3), P1-C14 182.8(3), P2-C27 182.0(3), P2-C33 182.6(3). Angles (deg.): N1-C1-N2 116.3(2), N1-C1-P1 126.3(2), N2-C1-P1 117.4(2), C1-P1-C8 103.7(1), C1-P1-C14 103.3(1), C8-P1-C14 104.9(1), N3-C20-N4 116.1(2), N3-C20-P2 117.4(2), N4-C20-P2 126.4(2), C20-P2-C27 104.2(1), C20-P2-C33 103.4(1), C27-P2-C33 105.9(1).

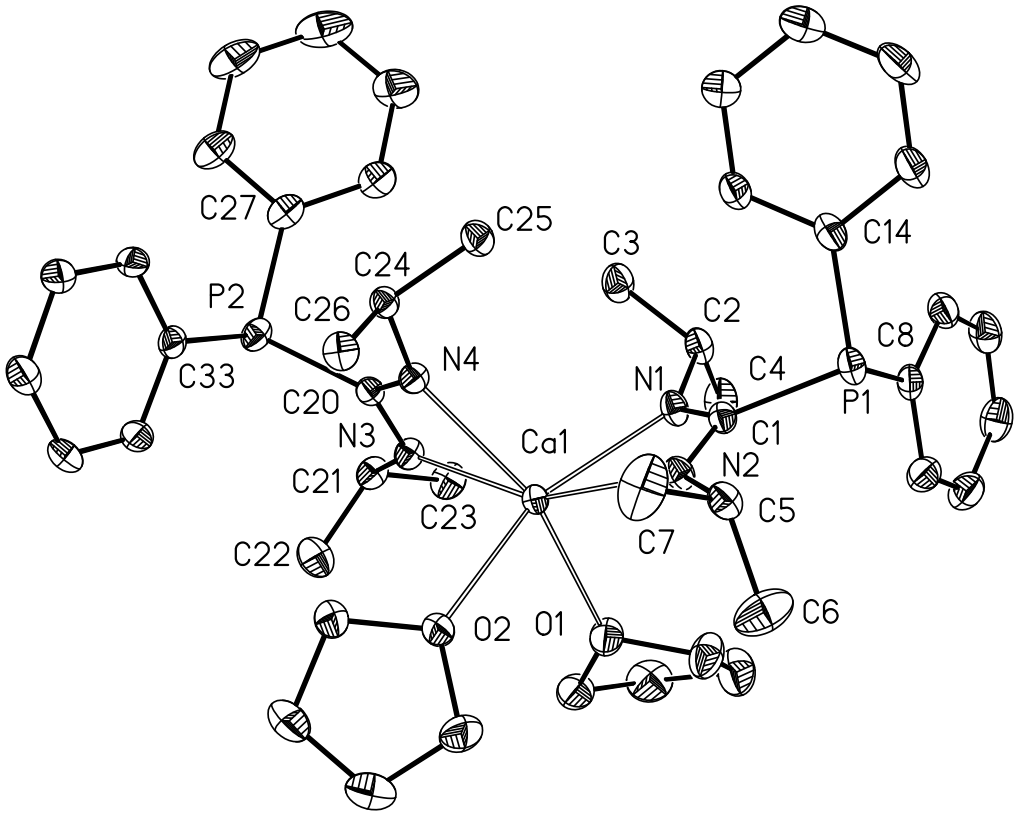
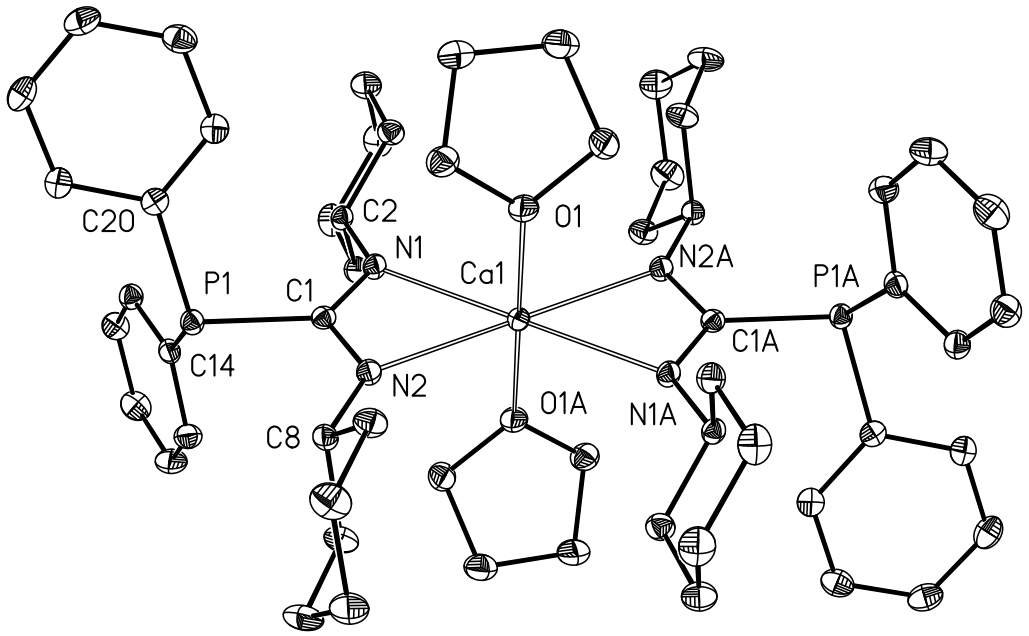


Figure 3.15: Molecular structure and numbering scheme of $[(thf)_2Ca\{CyNC(PPh_2)NCy\}_2]$ (**16**). Symmetry-related atoms (-x, -y, -z+1) are marked with the letter "A". The ellipsoids represent a probability of 40%, hydrogen atoms are omitted for clarity reasons. Selected bond lengths (pm): Ca1-N1 241.3(1), Ca1-N2 243.5(2), Ca1-O1 241.1(1), C1-P1 190.6(2), C1-N1 132.4(2), C1-N2 133.8(2), N1-C2 146.2(2), N2-C8 145.7(2), P1-C14 183.1(2), P1-C20 183.3(2). Angles (deg.): N1-C1-N2 116.1(2), N1-C1-P1 126.7(1), N2-C1-P1 117.2(1), C1-P1-C14 103.66(8), C1-P1-C20 104.75(8), C14-P1-C20 105.79(8).



Regardless of the *cis* or *trans* arrangement of the phospha(III)guanidinate ligands, they show very similar and characteristic structural features. The carbon atoms of the 1,3-diazaallyl systems are in a planar environment allowing a delocalization of the anionic charge. Therefore both CN bonds show similar values characteristic for CN multiple bonds with bond orders of approximately 1.5. The C-N bond lengths to the N-bound alkyl groups are more than 10 pm larger. The phosphorus atoms are in trigonal pyramidal environments. Unexpected large P-C distances (av. 190.6 pm) are observed for the bonds to the allylic carbon atoms whereas the P-C bonds to the phenyl groups adopt typical values for P-C single bonds (av. 182.9 pm). The pyramidal coordination sphere of the phosphorus atom and the large P-C distance to the allyl unit exclude attractive interactions. This elongation of the P-C bonds

cannot exclusively be caused by steric repulsion but have to be explained by electrostatic repulsion between phosphorus and carbon. This effect increases with decreasing electronegativity of the metal atom. Strong electropositive metals such as calcium lead to a stronger elongation than less electropositive metals such as aluminium [154] or $Mo(CO)_4$ and $W(CO)_4$ fragments [152].

In Table 3.6 selected structural parameters of **15** and **16** are listed in comparison to related compounds such as benzamidinates and guanidinates. In general, the hydrogen atom is located at a nitrogen atom leading to two significantly different N-C bond lengths (N1-C single bond, N2=C double bond) [152, 157]. In complexes with electropositive metals the phospha(III)guanidinate acts as a bidentate ligand *via* the nitrogen donors with lithium being an exception [153, 154].

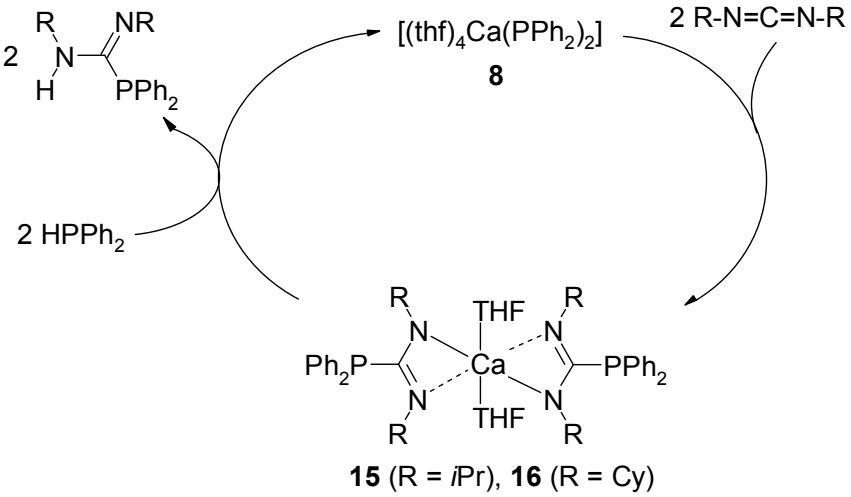
Table 3.6: Comparison of selected structural parameters of **15** and **16** with related compounds containing 1,3-diazaallyl units (Cy cyclohexyl, *i*Pr isopropyl, Me methyl, Ph phenyl).

Compound	C.N.(M)	Donors	R	R'	M-N	R-C	N1-C	N2-C	Ref.
R-C(=NR')N(H)R'	1 (H)	N1	PPh_2	Cy		187.8(2)	136.4(2)	128.6(2)	[152]
R-C(=NR')N(H)R'	1 (H)	N1	PPh_2	*i*Pr		188.2(3)	137.2(3)	126.8(3)	[152]
R-C(=NR')N(H)R'	1 (H)	N1	PCy_2	*i*Pr		188.2(3)	137.5(3)	127.8(3)	[157]
R-C(=NR')N(H)R'	1 (H)	N1	$P(S)Ph_2$	Cy		189.1(2)	136.1(2)	127.9(2)	[157]
R-C(=NR')N(H)R'	1 (H)	N1	$P(Se)Ph_2$	Cy		188.1(1)	136.0(2)	127.9(2)	[157]
[{R-C(=NR')N(H)R'}$_2$CuBr]	3 (Cu), 1 (H)	P [a]	PPh_2	*i*Pr		188.1(2)	136.9(3)	127.8(3)	[155]
[{R-C(=NR')N(H)R'}BH_3]	4 (B), 1 (H)	P [b]	PPh_2	Cy		187.4(2)	136.7(3)	128.0(3)	[157]
[{R-C(=NR')N(H)R'}$Mo(CO)_4$]	6 (Mo), 1 (H)	N2, P	PPh_2	Cy	231.3(2)	185.4(2)	134.2(2)	130.4(2)	[152]
[{R-C(=NR')N(H)R'}$W(CO)_4$]	6 (W), 1 (H)	N2, P	PPh_2	Cy	229.9(2)	185.3(2)	134.3(3)	130.1(3)	[152]
[{R-C(=NR')NR'}Li(tmeda)]	4 (Li)	N1, P	PPh_2	*i*Pr	192.7(5)	189.2(3)	135.4(4)	129.9(4)	[153, 154]
[{R-C(=NR')NR'}$AlMe_2$]	4 (Al)	N1, N2	PPh_2	*i*Pr	192.8(2)	186.9(2)	133.7(3)	133.6(3)	[154]
[{R-C(=NR')NR'}$AlPh_2$]	4 (Al)	N1, N2	PPh_2	*i*Pr	192.5(2)	188.6(2)	133.6(2)	133.9(2)	[154]
[{R-C(=NR')NR'}Ca(Nacnac)(thf)]	5 (Ca)	N1, N2	PPh_2	*i*Pr	241.7	191.9(2)	133.1(2)	132.7(2)	[160]
[{R-C(=NR')NR'}$_2$Ca(OEt_2)]	5 (Ca)	N1, N2	$N(SiMe_3)_2$	Cy	238.4	145.5(3)	132.5(4)	132.1(4)	[200]
[{R-C(=NR')NR'}$_2$Ca($thf)_2$] **15**	6 (Ca)	N1, N2	PPh_2	*i*Pr	242.5	191.0(2)	133.3(3)	132.1(3)	[148]
[{R-C(=NR')NR'}$_2$Ca($thf)_2$] **16**	6 (Ca)	N1, N2	PPh_2	Cy	242.4	190.6(2)	133.8(2)	132.4(2)	[148]
[{R-C(=NR')NR'}$_2$Ca($thf)_2$]	6 (Ca)	N1, N2	Ph	$SiMe_3$	243.1	149.2(4)	132.2(4)	131.7(4)	[199]

[a] The copper atom coordinates to two phosphorus atoms; the hydrogen atom binds to N1. [b] The BH_3 unit coordinates to the phosphorus atom; the hydrogen atom binds to N1.

Alkali and early transition metal complexes show a high catalytic activity in hydrophosphanylation reactions. Therefore we investigated these complexes in the catalytic hydrophosphanylation of carbodiimides. First hints of catalytic activity were obtained from the observation, that despite the stoichiometric ratio of starting $[(thf)_4Ca(PPh_2)_2]$ and RN=C=NR varying amounts of already well-known [152] free phospha(III)guanidine HN(R)-C(PPh_2)=NR were obtained (Fig. 3.16). Therefore, we investigated the reaction of $HPPh_2$ with RN=C=NR in THF at room temperature in the presence of 1 mol-% and 3 mol-% of **15** and **16**. A catalytic cycle for the formation of these phospha(III)guanidines is shown in Figure 16. However, the catalytic activity of the calcium compounds **15** and **16** is much smaller than for other reported procedures (e.g. [158, 159,160]). After two hours significant amounts of $HPPh_2$ were still observed by ^{31}P NMR spectroscopy whereas the bis(trimethylsilyl)amides of calcium [160], lithium and potassium [158, 159] gave a quantitative conversion within a few minutes at room temperature.

Figure 3.16: Proposed catalytic cycle for a calcium-mediated hydrophosphanylation of carbodiimides yielding the phospha(III)guanidines in a side reaction.



15 (R = *i*Pr), **16** (R = Cy)

A reason for the reduced catalytic activity of **15** and **16** compared to $LiN(SiMe_3)_2$, $KN(SiMe_3)_2$ and $Ca\{N(SiMe_3)_2\}_2$ is the steric shielding of the metal center. In **15** and **16** the metal atoms show distorted octahedral environments with rather small Ca-N and Ca-O bond lengths whereas in the bis(trimethylsilyl)amide complexes a coordination number of four is realized in the THF adduct $[(thf)_2Ca\{N(SiMe_3)_2\}_2]$ [201, 147i]. The rather high melting points of **15** and **16** also support that THF is bound rather tightly impeding the liberation of THF molecules from these complexes.

3.5. Synthesis and X-ray Structures of Calcium and Strontium Diphenylphosphinates of the Type $(L)_nM[E_2PPh_2]_2$ (E= S, Se) (L= THF).

Treatment of lithiated diphenylphosphane with 1 equiv of elemental Se in the presence of the Lewis base TMEDA (tetramethylethylenediamine) led to insertion of a Se atom into the P-Li bond yielding $[Ph_2PSeLi•TMEDA]_2$. This lithium selenophosphinite was then oxidized by addition of another equivalent of Se to give the lithium diselenophosphinate $[Ph_2PSe_2Li•TMEDA•THF]$. However, better yields of diselenophosphinates were achieved from the reaction of the initially lithiated diphenylphosphane with 2 equiv of Se [167]. Potassium and indium diselenophosphinate $[K(Se_2PPh_2)(THF)_2]_2$ and $[In(Se_2PPh_2)_3]$ were obtained in 79% yield from the reaction of potassium diphenylphosphanide with 2 equiv of grey selenium powder in THF/toluene and the metathesis reactions with $InCl_3$ [169] (equation 15). Complexes of the heavier chalcogens were obtained and reported upon treatment of $K(PR_2BH_3)$ with elemental sulfur or grey selenium in THF (equation 16) [174]. Zukerman and Ionel also reported the synthesis and characterization of antimony and indium dithiophosphinates $M(S_2PR_2)_3$ (M= Sb, R= Et; M= In, R= Me, Ph) [178b].

$$3\ KPPh_2 \xrightarrow[THF]{6\ Se} 3\ [K(Se_2PPh_2)(THF)_2]_2 \xrightarrow[-3\ KCl]{InCl_3} In(Se_2PPh_2)_3 \qquad (15)$$

$$K(PR_2BH_3) \xrightarrow[THF]{+E} K(EPR_2BH_3)$$

E= S, Se,
R= Ph, tBu

(16)

In a similar procedure as described [167] and also in accordance with literature procedures [202], the reaction of calcium and strontium diphenylphosphanide with 4 equivalents of elemental sulfur and grey selenium in THF gave the oxidation products, calcium and strontium diphenylphosphinates $(thf)_3Ca[S_2PPh_2]_2$ **17**, $(thf)_3Sr[S_2PPh_2]_2$ **18**, $(thf)_2Ca[Se_2PPh_2]_2$ **19**, and $(thf)_3Sr[Se_2PPh_2]_2$ **20,** respectively, in high yields according to equation 17.

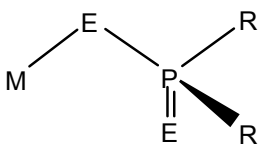
$$(THF)_4M(PPh_2)_2 \xrightarrow[THF]{+E} (THF)_nM(E_2PPh_2)_2$$

M =	E =
Ca	S, n=3 (**17**)
Sr	S, n=3 (**18**)
Ca	Se, n=2 (**19**)
Sr	Se, n=3 (**20**)

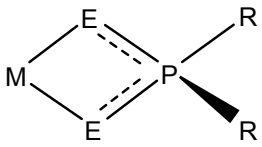
(17)

All of the complexes **17** to **20** were isolated as colorless air stable crystalline solids. When we reacted calcium and strontium phosphanides with tellurium, the complexes decomposed directly and also lost tellurium upon contact with air or with silicone grease. It is interesting to note that tellurium complexes are not very stable and can neither be isolated nor structurally characterised. This finding is in accordance with the related triorganophosphane telluride $TePPh_2CH_3$, which also forms only as a minor component in a dynamic equilibrium when the phosphane PPh_2CH_3 is treated with excess of tellurium in thf solution [202].

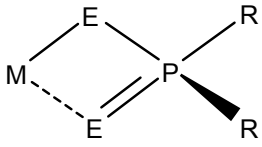
Insertion of Se into polar R-M bonds have been known for many years [203] and have proved to be one of the most valuable methods for the synthesis of organic selenolates since they do not require the use of readily oxidized selenols as starting materials [166]. Indeed, reactions of metalated diorganylphosphanides with elemental chalcogens yielding dichalcogenophosphinates have already been employed in the synthesis of mixed chalcogenotellurophosphinates [204]. Another published route to diselenophosphinates is the reaction of chlorophosphanes, R_2PCl, with selenium giving $R_2P(Se)Cl$ and then with 2 equiv of NaSeH yielding the sodium salt of the diselenophosphinate and hydrogen selenide [175,205]. Diphenylphosphinate ligands should be able to show different coordination patterns. They can behave as monodentate (**A**), isobidentate (symmetric) (**B**), anisobidentate (asymmetric) (**C**) ligands.



A



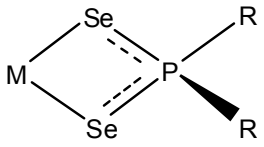
B



C

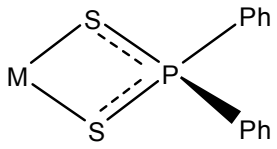
Monodentate behaviour is rare but is known in $Ph_3Sn\text{-}SP(S)(OEt)_2$ [206] whereas iso- and anisobidentate coordination are found in the closely related organotin compounds $Ph_2Sn[S_2P(OPr^i)_2]_2$ [207] and $Ph_2Sn[S_2P(OEt)_2]_2$ [208], respectively.

The molecular structures of $Ca(S_2PPh_2)_2$ **17**, $Sr(S_2PPh_2)_2$ **18**, $Ca(Se_2PPh_2)_2$ **19**, and $Sr(Se_2PPh_2)_2$ **20** are illustrated in figures 3.17-3.20. The solid state structures of **19** and **20** are monomeric with the six-coordinate calcium and hepta-coordinate strontium cations coordinated symmetrically to the phosphinate ligands; the coordination spheres are saturated by 2 THF and 3 THF molecules, respectively (figures 3.19, 3.20). The solid state structures of three other complexes containing this ligand have previously been reported: $[Na_2(Se_2PPh_2)\cdot THF\cdot 5THF]$ [176], $[Ni(Se_2PPh_2)_2]$ [209,210], and $Cp_2Ti(Se_2PPh_2)]$ [211]. As in these previously reported examples the four P-Se bonds in **19** show approximately the same lengths [2.1621(2), 2.153(2), 2.155(2) and 2.158 (2)] and correspond to a value between those expected for a P-Se single [167] and double bond [212]. The bond lengths of complex **20** [2.1547(15), 2.1554(14), 2.1549(16) and 2.1464(17)] also lie between those expected for P-Se single [167] and double bonds [212], indicating complete delocalization of the negative charge within the PSe_2 units. Thus, the ligands can be described as isobidentate.



The complex $Sr(Se_2PPh_2)_2(THF)_3$ **20** (figure 3.20) displays a distorted pentagonal bipyramidal coordination sphere, with quite similar Sr-Se bonds and basically isobidentate diselenophosphinate ligands. In complex **19** the calcium atom shows a distorted octahedral environment with two THF molecules in a cis arrangement. The small endocyclic Se-Ca-Se bond angles in the four-membered chelate rings (74.82-74.90°) cause the observed distortions of the octahedral coordination sphere. The 7-coordinate Sr cation in **20** is located slightly asymmetric between the four Se bases of the diselenophosphinates [Se1A-Sr1A 3.1812(9) Å, Se2A-Sr1A 3.1595(8) Å, Se3A-Sr1A 3.1617(9) Å, Se4A-Sr1A 3.1804(7) Å], these Sr-Se bonds are longer than those observed in **19** with six-coordinate calcium atoms [Se1A-Ca1A 2.9799(15) Å, Se2A-Ca1A 2.9755(15) Å, Se3A-Ca1A 2.9580(15) Å, Se4A-Ca1A 2.9985(16) Å] resembling the larger size of the Sr cations.

The solid state structures of **17** and **18** are monomeric with the calcium and strontium cations showing the coordination numbers of 7 (figures 3.17, 3.18). The structures $M(S_2PPh_2)_2(THF)_3$ (M= Ca and Sr) display distorted pentagonal bipyramidal coordination spheres for the alkaline earth metal atoms, with nearly equal Ca-S and Sr-S bonds and basically isobidentate (symmetric) dithiophosphinates ligands, forming four-membered chelate rings of type **B**. The phosphorus atoms in both complexes are distorted tetrahedrally surrounded with S-P-S angles 113.82(5) and 114.37(5), 115.31(12) and 115.97(13), respectively.

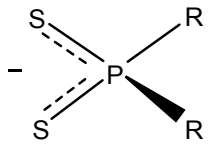


B

The differences Δ(P-S) and Δ(M-S) observed between likewise pairs of bonds within the same chelate MS_2P ring can be taken as a measure of asymmetry. Thus, in $Ca(S_2PPh_2)_2(THF)_3$ and $Sr(S_2PPh_2)_2(THF)_3$, the Ca-S and Sr-S interatomic distances within CaS_2P and SrS_2P chelating ring do not differ by more than 0.033 Å and 0.040 Å, respectively, and the P-S interatomic distances differ less than 0.0081 Å in the Ca and 0.014 Å in the Sr derivatives. Thus, the ligands can be described as isobidentate. Another important set includes the S-Ca-S and S-Sr-S bond angles of the pentagonal bipyramid. In a regular pentagonal plane, all these values are expected to be 72°. The small bites S-Ca-S and S-Sr-S in the four-membered chelate rings (69.8-69.83º and 67.51- 67.69º) are the cause of the observed distortions of the coordination sphere, but are rather close to the ideal value of a regular pentagonal plane. The apical bases should show a S-M-S angle of 180°, however, due to the ring strain smaller values of 140.76 are observed.

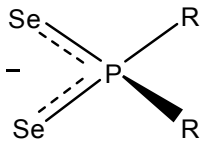
Comparisons with other structures:

In the calcium and strontium dithiophosphinate cases, the structures available for comparison are those of dithiophosphinates, $NaS_2PEt_2•2H_2O$ [213], $In[S_2P(Me)_2]_3$ [178], $In(S_2PEt_2)_3$ [214], $In(S_2PPh_2)_3$ [178] and thiophosphinate $Sb(S_2PPh_2)_3$ [215]. In $Ca(S_2PPh_2)_2(THF)_3$ and $Sr(S_2PPh_2)_2(THF)_3$, the ligand is more symmetrically coordinated, with minor Δ(P-S) and Δ(M-S) and quite similar to that of $NaS_2PEt_2•2H_2O$, $In[S_2P(Me)_2]_3$, $In(S_2PEt_2)_3$ and $In(S_2PPh_2)_3$, with comparable Δ(P-S) and Δ(Ca-S) and Δ(Sr-S) values (Table 3.7), but it is different to that of $Sb(S_2PPh_2)_3$. It could be described as a coordinated anion, **Y**.



Y

The structures of $Ca(Se_2PPh_2)_2(THF)_2$ **19** and $Sr(Se_2PPh_2)_2(THF)_3$ **20**, the phosphorus atoms in both **19** and **20** are distorted tetrahedral with Se-P-Se angles of 114.08(8) and 114.11(8), 114.38(7) and 114.60(7), respectively, and Ph-P-Ph angles of 103.6(3) and 103.2(3), 104.4(3) and 104.5(4), respectively. In $Ca(Se_2PPh_2)_2(THF)_2$ and $Sr(Se_2PPh_2)_2(THF)_3$, the ligand is more symmetrically coordinated, with minor Δ(P-Se) and Δ(M-Se) values and quite similar to that of $Na_2[Se_2PPh_2]_2 \bullet THF \bullet 5H_2O$**,** $Ni(Se_2P^tBu_2)_2$, $Ni(Se_2P^iPr_2)_2$, $Cp_2Ti(Se_2PPh_2)$ and $In(S_2PPh_2)_3 \bullet L$ (L=THF, Tol.), with comparable Δ(P-Se) and Δ(Ca-Se) and Δ(Sr-Se) values (Table 3.8). It could be described as a coordinated anion, **Z**.



Z

As a facit it can be concluded that strongly electropositive metals coordinate predominantly in a more symmetrical manner whereas less electropositive elements prefer an unsymmetric coordination mode.

Figure 3.17: Molecular structure and numbering scheme of $(thf)_3Ca[S_2PPh_2]_2$ **17**. The ellipsoids represent a probability of 40%, H atoms are neglected for clarity reasons. Selected bond lengths (pm): Ca1-S1 291.18(10), Ca1-S2 292.17(9), Ca1-S3 294.34(10), Ca1-S4 291.03(10), P1-S1 199.60(10), P1-S2 198.79(11), P2-S3 199.39(11), P2-S4 199.30(10); angles (deg.): S1-Ca1-S2 69.80(2), S4-Ca1-S3 69.83(2), S2-Ca1-S3 140.87(3), S4-Ca1-S1 140.98(3), S4-Ca1-S2 71.47(2), S1-Ca1-S3 149.17(3), S2-P1-S1 113.82(5), S4-P2-S3 114.37(5),P1-S1-Ca1 87.83(4), P1-S2-Ca1 87.70(3),P2-S4-Ca1 88.37(4),P2-S3-Ca1 87.43(3)

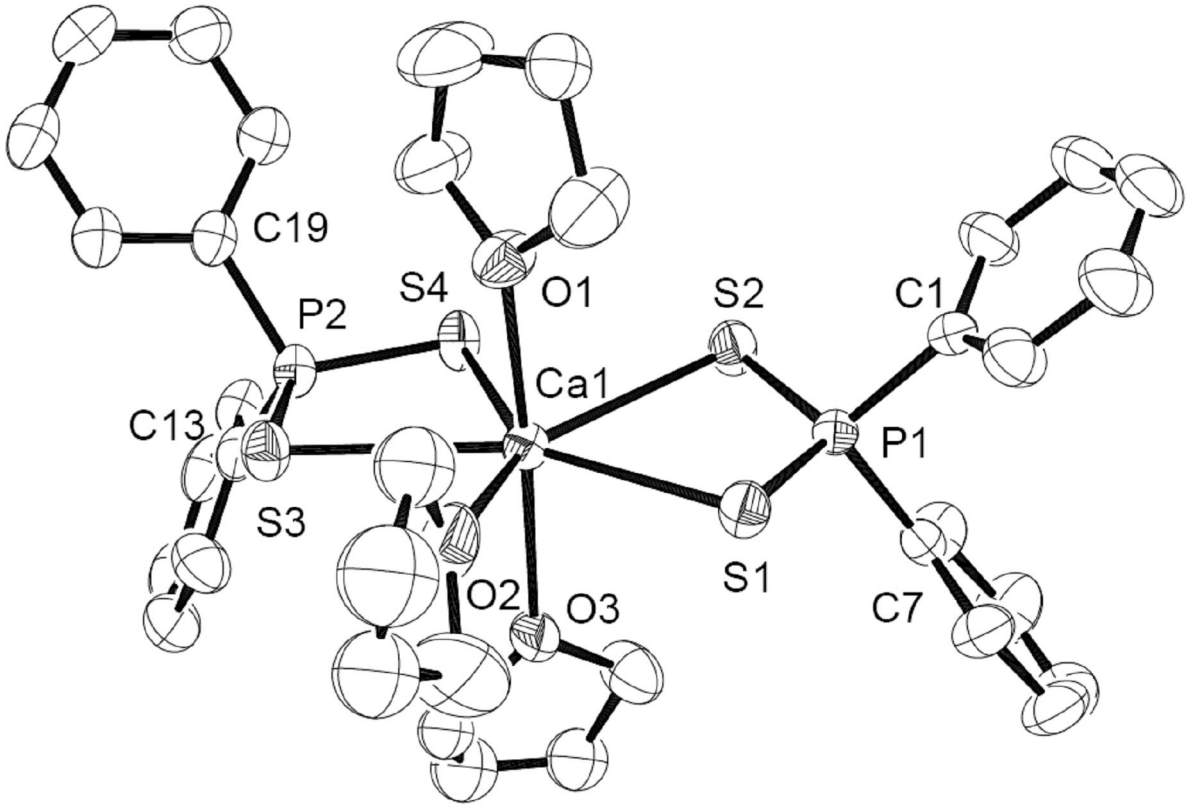


Figure 3.18: Molecular structure and numbering scheme of $(thf)_3Sr[S_2PPh_2]_2$ **18**. The ellipsoids represent a probability of 40%, H atoms are neglected for clarity reasons. Selected bond lengths (pm): Sr1A-S1A 303.1 (2), Sr1A-S2A 302.4(2), Sr1A-S3A 305.9(2), Sr1A-S4A 301.9(2), P1A-S1A 199.8(3), P1A-S2A 198.4(3), P2A-S3A 199.9(3), P2A-S4A 199.2(3). Angles (deg.): S1A-Sr1A-S2A 67.51(5), S4A-Sr1A-S3A 67.69(6), S2A-Sr1A-S3A 140.76(6), S4A-Sr1A-S1A 141.01(6), S4A-Sr1A-S2A 73.54(6), S1A-Sr1A-S3A 151.16(6), S2A-P1A-S1A 115.31(12), S4A-P2A-S3A 115.97(13),P1A-S1A-Sr1A 57.94(7), P1A-S2A-Sr1A 57.76(8),P2A-S4A-Sr1A 57.42(8),P2A-S3A-Sr1A 58.56(8)

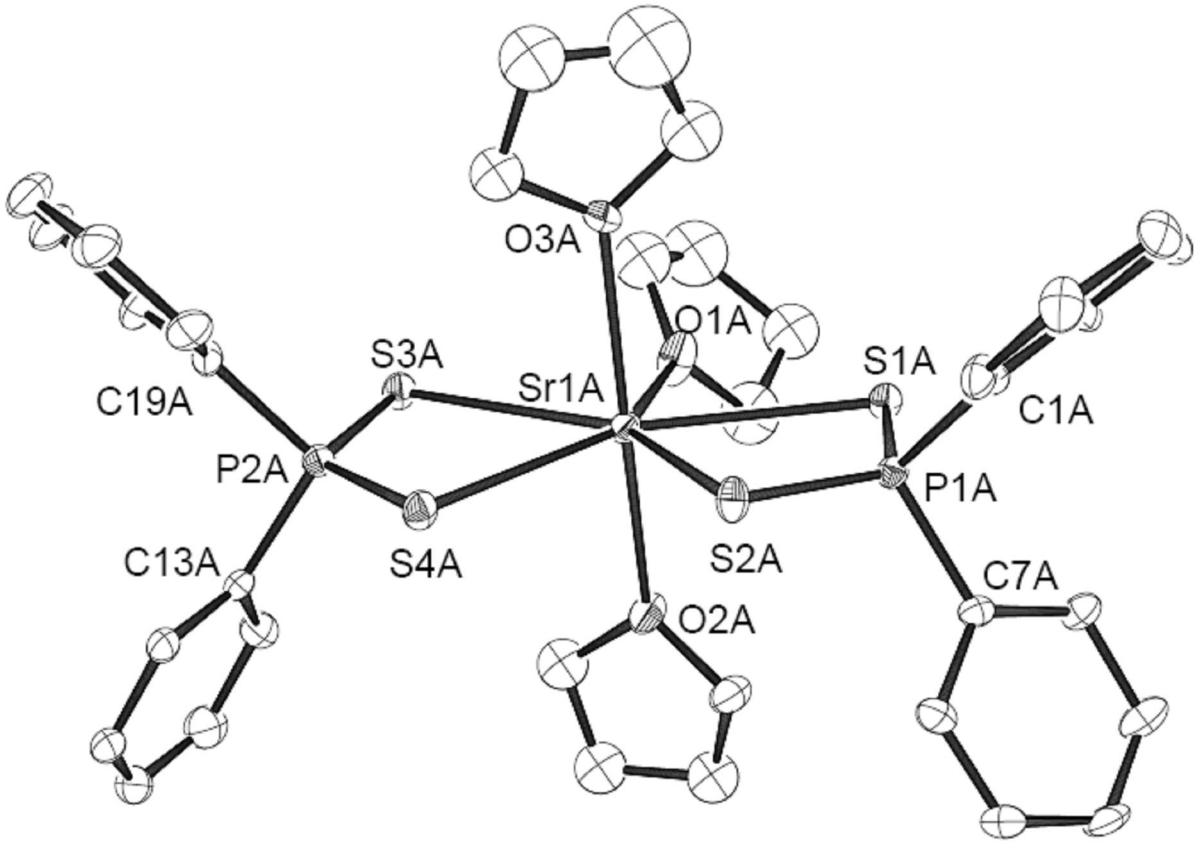


Figure 3.19: Molecular structure and numbering scheme of $(thf)_3Ca[Se_2PPh_2]_2$ **19.** The ellipsoids represent a probability of 40%, H atoms are neglected for clarity reasons. Selected bond lengths (pm): Ca1A-Se1A 297.99 (15), Ca1A-Se2A 297.55(15), Ca1A-Se3A 295.80(15), Ca1A-Se4A 299.85(16), P1A-Se1A 216.23(16), P1A-Se2A 215.29(17), P2A-Se3A 215.47(18), P2A-Se4A 215.81(17). Angles (deg.): Se1A-Ca1A-Se2A 74.90(4), Se4A-Ca1A-Se3A 74.82(4), Se2A-Ca1A-Se3A 99.79(4), Se4A-Ca1A-Se1A 106.18(4), Se4A-Ca1A-Se2A 96.48(4), Se1A-Ca1A-Se3A 174.64(5), Se2A-P1A-Se1A 114.11(8), Se4A-P2A-Se3A 114.08(8),P1A-Se1A-Ca1A 85.33(5), P1A-Se2A-Ca1A 85.60(5),P2A-Se4A-Ca1A 84.33(5),P2A-Se3A-Ca1A 85.40(6)

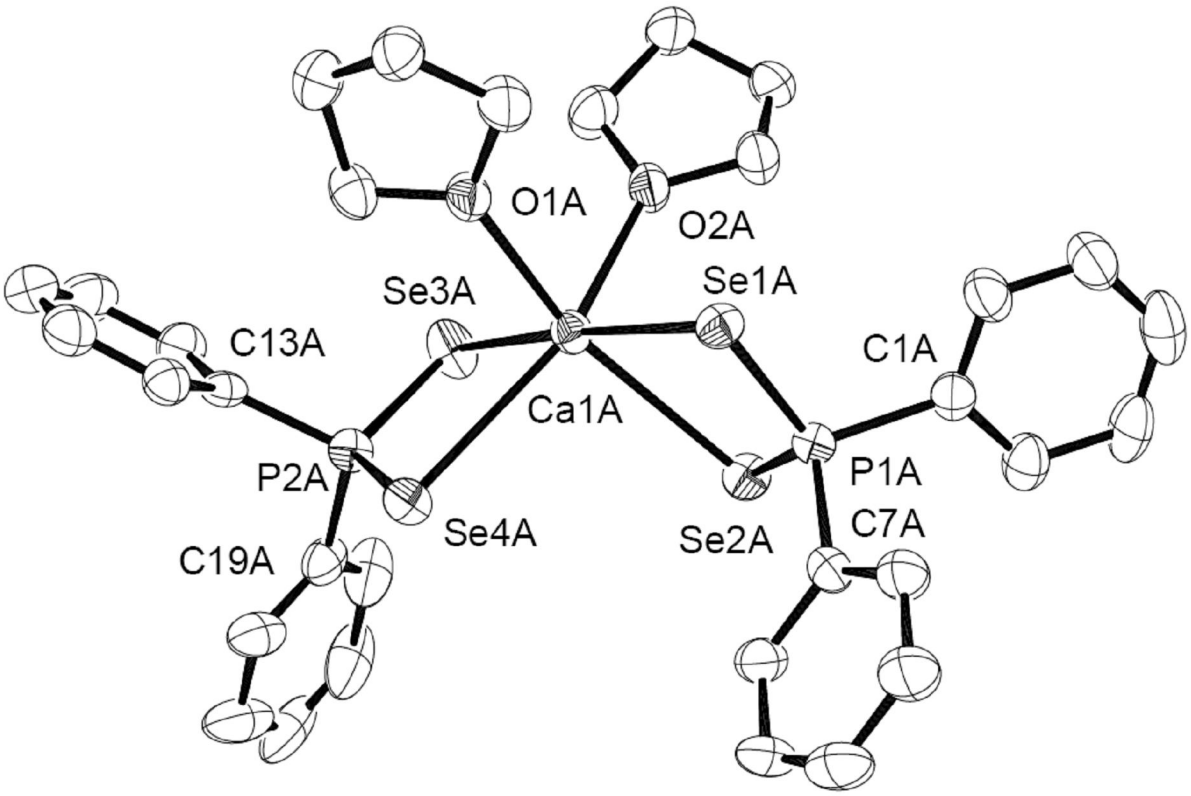


Figure 3.20: Molecular structure and numbering scheme of $(thf)_2Sr[Se_2PPh_2]_2$ **20**. The ellipsoids represent a probability of 40%, H atoms are neglected for clarity reasons.Selected bond lengths (pm): Sr1A-Se1A 318.12 (9), Sr1A-Se2A 315.95(8), Sr1A-Se3A 316.17(9), Sr1A-Se4A 318.04(7), P1A-Se1A 215.47(15), P1A-Se2A 215.54(16), P2A-Se3A 215.49(14), P2A-Se4A 214.46(17). Angles (deg.): Se1A-Sr1A-Se2A 69.781(19), Se4A-Sr1A-Se3A 69.503(19), Se2A-Sr1A-Se3A 135.12(2), Se4A-Sr1A-Se1A 131.75(2), Se4A-Sr1A-Se2A 71.305(18), Se1A-Sr1A-Se3A 155.08(2), Se2A-P1A-Se1A 114.60(7), Se4A-P2A-Se3A 114.38(7),P1A-Se1A-Sr1A 86.35(5), P1A-Se2A-Sr1A 86.89(4),P2A-Se4A-Sr1A 87.49(4),P2A-Se3A-Sr1A 87.84(5)

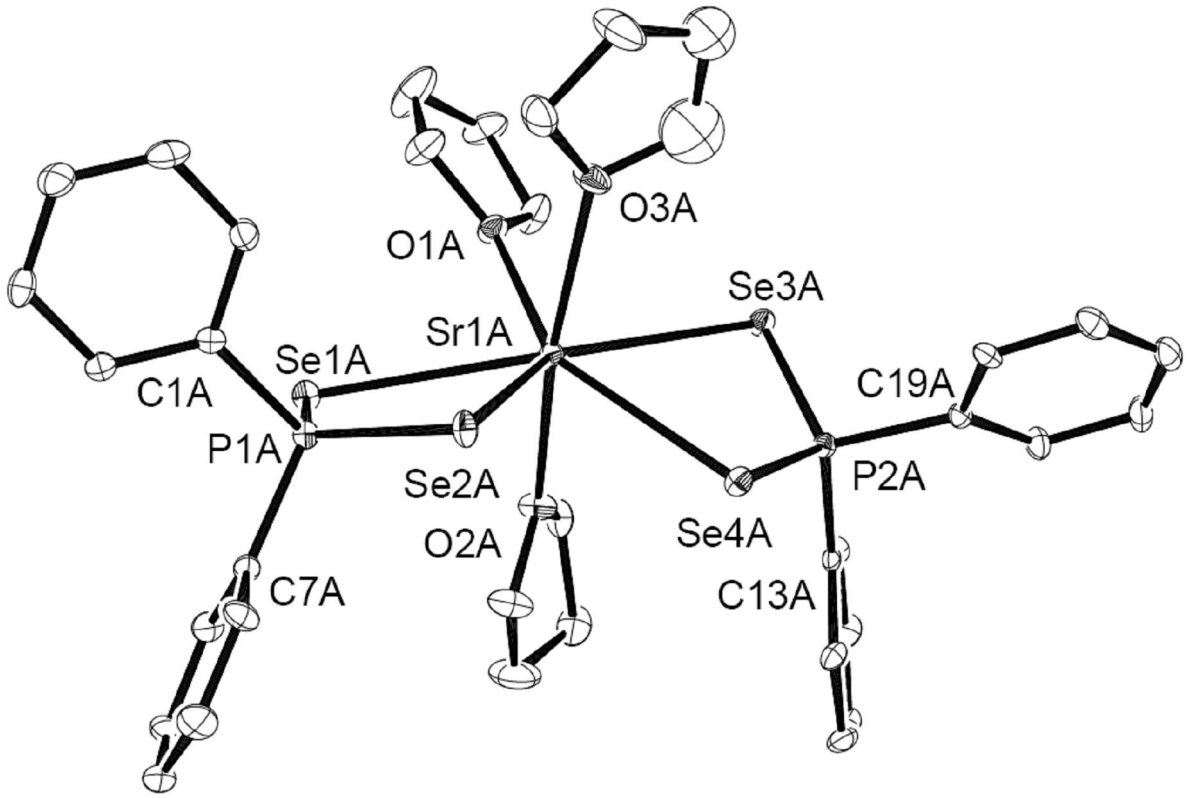


Table 3.8: Comparison of P-Se and M-Se bond asymmetries in MSe_2 chelate rings (M = Ca, Sr).

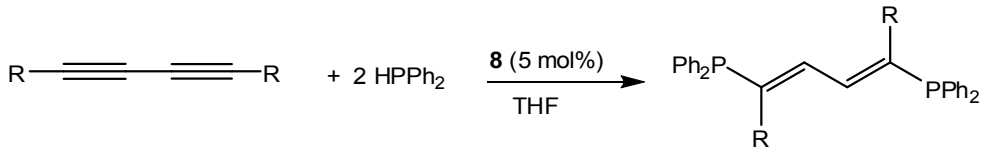
Complex	**P-Se Bond lengths (Å)**	**Δ(P-Se)**	**M-Se Bond lengths (Å)**	**Δ(M-Se)**	**Ref.**
$Ca(Se_2PPh_2)_2(THF)_2$	2.1623(16) 2.1529(17) 2.1581(18) 2.1547(17)	0.0094 0.0034	2.9799 (15) 2.9755(15) 2.9985(15) 2.9580(16)	0.0044 0.0405	This work
$Sr(Se_2PPh_2)_2(THF)_3$	2.1554(15) 2.1547(16) 2.1549(14) 2.1446(17)	0.0007 0.0103	3.1812 (9) 3.1595(8) 3.1804(9) 3.1617(7)	0.0217 0.0187	This work
$Cp_2Ti(Se_2PPh_2)$	2.151(4) 2.151(4)	0.000	2.764(3) 2.754(3)	0.010	[211]
$Ni(Se_2P\ ^tBu_2)_2$	2.1809(2) 2.1777(2) 2.1785(2) 2.1782(2)	0.0032 0.0003	2.3520(9) 2.3482(9) 2.3467(9) 2.3408(9)	0.0038 0.0059	[209]
$Ni(Se_2P\ ^iPr_2)_2$	2.1728(6) 2.1703(6) 2.1728(6) 2.1703(6)	0.0025 0.0025	2.3591(3) 2.3566(3) 2.3591(3) 2.3566(3)	0.0025 0.0025	[209]
$[LiSe_2PPh_2]\cdot THF\cdot TMEDA$	2.147(1) 2.141(1)	0.006	2.940(6) 2.848(7)	0.092	[167]
$Na_2[Se_2PPh_2]_2\bullet THF\bullet 5H_2O$	2.156(1) 2.152(1) 2.161(1) 2.142(1)	0.004 0.019	2.984(2)	-	[176]
$[In(Se_2PPh_2)_3]\cdot THF$	2.179 2.168 2.174 2.170 2.175 2.168	0.011 0.004 0.007	2.779 2.699 2.778 2.745 2.774 2.747	0.080 0.033 0.027	[169a]
$[In(Se_2PPh_2)_3]\cdot Tol.$	2.187 2.174 2.184 2.163 2.180 2.178	0.013 0.021 0.002	2.752 2.718 2.799 2.758 2.777 2.743	0.034 0.041 0.034	[169a]

Table 3.7: Comparison of P-S and M-S bond asymmetries in MS_2 chelate rings (M = Ca, Sr).

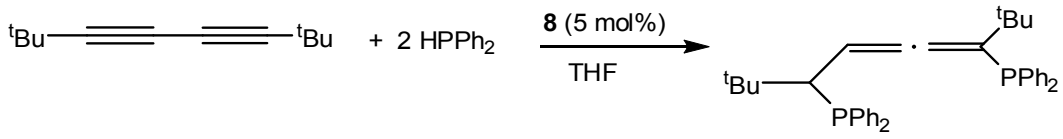
Complex	**P-S Bond lengths (Å)**	**Δ(P-S)**	**M-S Bond lengths (Å)**	**Δ(M-S)**	**Ref.**
$Ca(S_2PPh_2)_2(THF)_3$	1.9960(10) 1.9879(11) 1.9939(11) 1.9930(10)	0.0081 0.0009	2.9217(10) 2.9118(9) 2.9434(10) 2.9103(10)	0.0099 0.0331	This work
$Sr(S_2PPh_2)_2(THF)_3$	1.998(3) 1.984(3) 1.999(3) 1.992(3)	0.014 0.007	3.031 (2) 3.024(2) 3.059(2) 3.019(2)	0.007 0.040	This work
$NaS_2PEt_2•2H_2O$	2.034(2) 1.993(2)	0.041	3.001(1) 2.998(1)	0.003	[213]
$Sb(S_2PPh_2)_3$	2.048(1) 1.972(1) 2.089(1) 1.959(1) 2.044(1) 1.981(1)	0.076 0.130 0.063	2.978(1) 2.591(1) 3.187(1) 2.456(1) 2.923(1) 2.598(1)	0.387 0.731 0.325	[215]
$In(S_2PPh_2)_3$	2.015(8) 2.015(8) 2.018(9) 2.003(8) 2.012(7) 1.988(9)	0.000 0.015 0.024	2.622(6) 2.604(6) 2.588(6) 2.566(6) 2.621(6) 2.609(6)	0.018 0.022 0.012	[178a]
$In(S_2PMe_2)_3$	2.013(3) 2.004(3) 2.010(3) 2.007(3) 2.014(3) 2.009(3)	0.009 0.003 0.005	2.643(2) 2.628(2) 2.604(2) 2.602(2) 2.608(2) 2.599(2)	0.015 0.002 0.007	[178a]
$In(S_2PEt_2)_3$	2.012(2) 2.002(2) 2.029(2) 2.021(2) 2.023(2) 2.016(2)	0.010 0.008 0.007	2.638(1) 2.638(1) 2.621(1) 2.603(1) 2.628(1) 2.620(1)	0.000 0.018 0.008	[214]

Summary

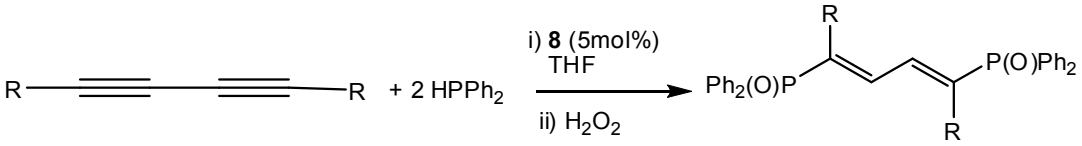
Hydrophosphanylation reactions of alkynes are catalyzed effectively by $[(thf)_4Ca(PPh_2)_2]$ (**8**). The reactions of alkyne and butadiynes with different substituents such as alkyl, aryl and trialkylsilyl with diphenylphosphane in THF in the presence of catalytic amounts of **8** (approx. 5 mol %) yield quantitatively the *cis*-addition products *trans*-1,2-diphenyl-1-diphenylphosphanylethene (**9**) and 1,4-bis(diphenylphosphanyl)-1,3-butadienes (**10**), respectively. The compounds **10b** and **10c** originate from a twofold *cis*-addition of $HPPh_2$ to the C≡C triple bonds of the appropriate butadiyne which give the *trans*/*trans*-isomer. In contrast to these derivatives, hexadiene **10a** crystallizes from the same reaction to give the *cis/cis*-isomer. Similar bindings are valid for the other butadiyne systems. 1,4-Dimesityl-1,4-bis(diphenylphosphanyl)butadiene (**10d**) contains no crystallographic symmetry elements. The phenyl groups in **10b** are oriented nearly perpendicular to the butadiene backbone and therefore, the π-systems of the phenyl groups and the butadiene unit show no interaction with each other. The behaviour of di-tert-butylbutadiyne (2,2,7,7-tetramethylocta-3,5-diene) seems to be very different from that of the other diynes. Thus, the latter butadiyne reacts with **8** at -78 °C to yield bis(diphenylphosphanyl)allene **12** with a yield of 70%. Next, we investigated the scope of the hydrophosphanylation of butadiynes and the oxidation of the formed products. Treatment of the butadiyne system with 2 equiv. of $HPPh_2$ in the presence of **8** (5 mol%) in THF at -78 °C for one hour, followed by oxidation with H_2O_2 affording the phosphane oxides **13a, 13b, 13c.**



R= Me (**10a**), Ph (**10b**), $SiMe_3$ (**10c**), Mes (**10d**)

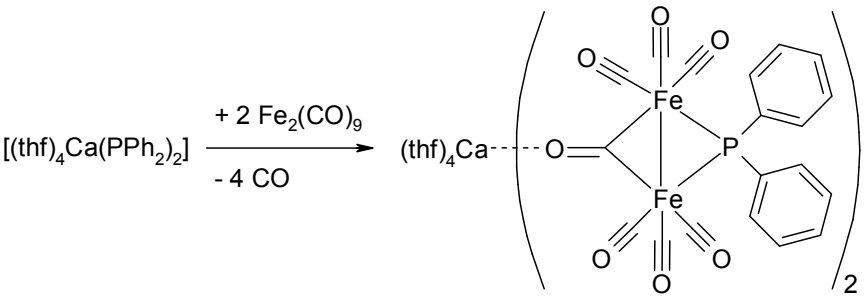


12



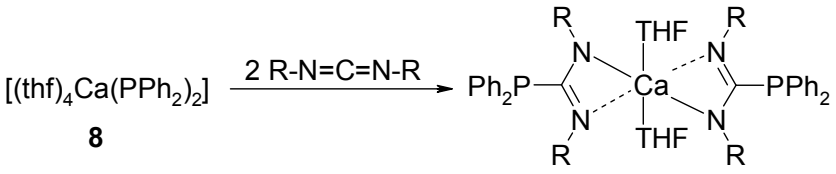
R = Me (**13a**), Ph (**13b**), $SiMe_3$ (**13c**)

The second part of the presented work is concerned with the preparation and characterization of $[(thf)_4Ca\{Fe_2(CO)_6(\mu\text{-}CO)(\mu\text{-}PPh_2)\}_2]$ (**14**). The reactions of $[(thf)_4Ca(PPh_2)_2]$ (**8**) with the iron carbonyls $Fe_2(CO)_9$ and $Fe_3(CO)_{12}$ in THF yield mixtures of iron carbonyl-containing phosphanides which transform upon prolonged heating into $[(thf)_4Ca\{Fe_2(CO)_6(\mu\text{-}CO)(\mu\text{-}PPh_2)\}_2]$ (**14**). The distorted octahedrally coordinated calcium atoms binds to four THF molecules (av. Ca-O 234.0 pm) and the bridging carbonyl ligand of the complex anions $\{Fe_2(CO)_6(\mu\text{-}CO)(\mu\text{-}PPh_2)\}^-$ (Ca-O 229.8(4), Fe-Fe 257.9(2) pm).



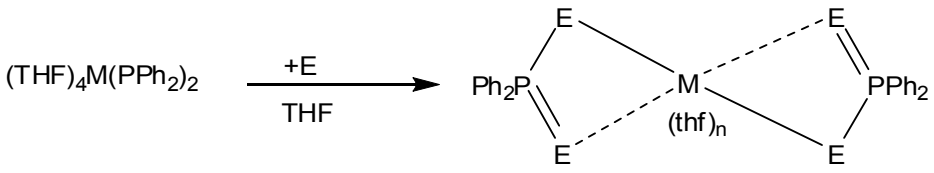
14

We extend the presented work in the synthesis and characterization of the phospha(III)guanidinates $[(thf)_2Ca\{RNC(PPh_2)NR\}_2]$. The reaction of $[(thf)_4Ca(PPh_2)_2]$ (**8**) with diisopropyl- and dicyclohexylcarbodiimides yields the phospha(III)guanidinates $[(thf)_2Ca\{RNC(PPh_2)NR\}_2]$ (R = isopropyl (**15**) and cyclohexyl (**16**). The metathesis reaction of $K\{RNC(PPh_2)NR\}$ with anhydrous CaI_2 also allows the synthesis of these phospha(III)guanidinate complexes **15** and **16**. For **15** a *cis* arrangement is observed whereas **16** crystallizes as the *trans* isomer. The phospha(III)guanidinates acts as a bidentate chelate bases with an average Ca-N distance of 242.5 pm. The C-P bond length between the PPh_2 fragment and the 1,3-diazaallyl unit is 190 pm, an unusual long distance. The complexes **15** and **16** show a moderate catalytic activity in hydrophanylation reactions of dialkylcarbodiimides with diphenylphosphane.



15 (R = *i*Pr), **16** (R = Cy)

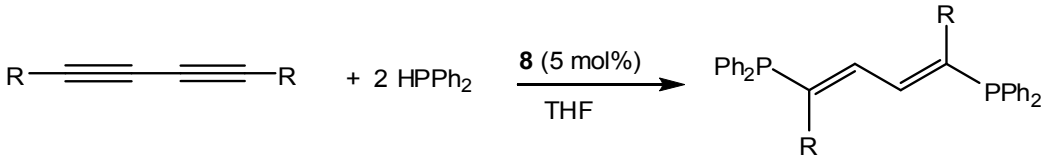
The reaction of calcium or strontium diphenylphosphanide with 4 equivalents of elemental sulfur or grey selenium in THF gave the oxidation products, calcium and strontium diphenylphosphinates $(thf)_3Ca[S_2PPh_2]_2$ **17**, $(thf)_3Sr[S_2PPh_2]_2$ **18**, $(thf)_2Ca[Se_2PPh_2]_2$ **19**, $(thf)_3Sr[Se_2PPh_2]_2$ **20,** respectively. All of the complexes **17** - **20** were isolated as colourless air stable crystalline solids. The solid state structures of **19** and **20** are monomeric with six-coordinate calcium and hepta-coordinate strontium cations coordinated symmetrically to the phosphinate ligands; the coordination spheres are saturated by 2 THF and 3 THF molecules, respectively. However, the solid state structures of **17** and **18** are monomeric with the calcium and strontium cations showing the coordination numbers of 7. The structures $M(S_2PPh_2)_2(THF)_3$ (M= Ca and Sr) display distorted pentagonal bipyramidal coordination spheres for the alkaline earth metal atoms, with nearly equal Ca-S and Sr-S bonds and basically isobidentate (symmetric) dithiophosphinate ligands, forming four-membered chelate rings. The phosphorus atoms in both complexes show distorted tetrahedral arrangements with S-P-S angles of 113.82(5) and 114.37(5), 115.31(12) and 115.97(13), respectively.



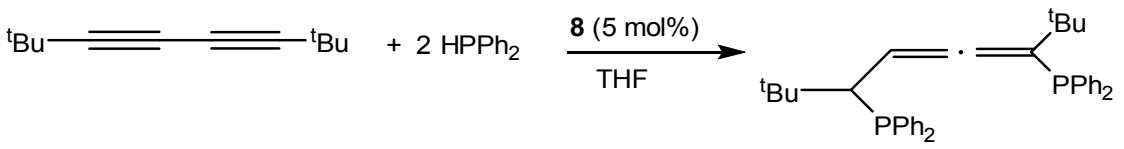
M =	E =
Ca	S, n = 3 (**17**)
Sr	S, n = 3 (**18**)
Ca	Se, n = 2 (**19**)
Sr	Se, n = 3 (**20**)

Zusammenfassung

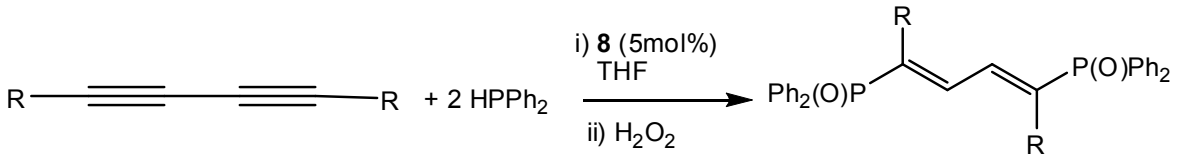
Die Verbindung $[(THF)_4Ca(PPh_2)_2]$ (**8**) ist ein leistungsfähiger Katalysator für die Hydrophosphanierung von Alkinen. So werden Alkine und Butadiine mit unterschiedlichen Substituenten, wie Alkyl, Aryl und Trialylsilyl, mit Diphenylphosphan in THF und in Gegenwart von **8** (ca. 5 mol%) quantitativ zu den *cis*-Additionsprodukten *trans*-1,2-Diphenyl-1-diphenylphosphanylethen (**9**) und 1,4-Bis(diphenylphosphanyl)-1,3-butadien (**10**) umgesetzt. Die Verbindungen **10b** und **10c** entstehen bei der zweifachen *cis*-Addition von $HPPh_2$ an die C-C Dreifachbindungen des entsprechenden Butadiins. Es bildet sich dabei das *trans/trans*-Isomer. Im Gegensatz dazu kristallisiert aus derselben Reaktion das *cis/cis*-Isomere des Hexadiens **10a**. Ähnliche Bindungsverhältnisse findet man auch in anderen Butadiinverbindungen. So enthält 1,4-Dimesityl-1,4-bis(diphenylphosphanyl)butadien (**10d**) keine kristallographischen Symmetrieelemente. Die Phenylgruppen in **10b** stehen senkrecht zum Butadienrückgrat, weshalb eine π-Wechselwirkung zwischen den Phenylringen und der Butadiengruppe auszuschließen ist. Das Reaktionsverhalten von Di-tert-butylbutadiin (2,2,7,7-tetramethylocta-3,5-dien) unterscheidet sich stark von dem der anderen Diine. Mit einer Ausbeute von 70 % reagiert diese Verbindung mit **8** bei -78 °C zum Bis(diphenylphosphanyl)allen **12**. Weiterhin wurden die Hydrophosphanylierungsprodukte hinsichtlich ihrer Oxidierbarkeit untersucht. Der Umsatz der Butadiine mit zwei Äquivalenten $HPPh_2$ in der Gegenwart katalytischer Mengen **8** (ca. 5 mol%) in THF und bei -78 °C und anschließender Oxidation mit H_2O_2 ergab die Phosphanoxide **13a-c**.



R= Me (**10a**), Ph (**10b**), $SiMe_3$ (**10c**), Mes (**10d**)

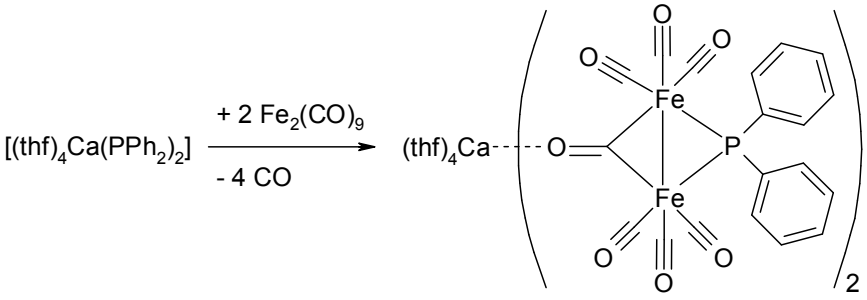


12



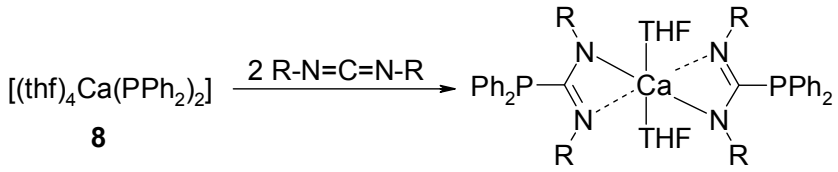
R = Me (**13a**), Ph (**13b**), $SiMe_3$ (**13c**)

Der zweite Teil der Arbeit beschäftigte sich mit der Darstellung und Charakterisierung von $[(THF)_4Ca\{Fe_2(CO)_6(\mu\text{-}CO)(\mu\text{-}PPh_2)\}_2]$ (**14**). Die Reaktion von $[(THF)_4Ca(PPh_2)_2]$ (**8**) mit den Eisencarbonylen $Fe_2(CO)_9$ und $Fe_3(CO)_{12}$ in THF führt zu Gemischen Eisencarbonyl-haltiger Phosphanide, welche durch längeres Erhitzen in $[(THF)_4Ca\{Fe_2(CO)_6(\mu\text{-}CO)(\mu\text{-}PPh_2)\}_2]$ (**14**) umgewandelt werden. Das verzerrt oktaedrisch koordinierte Calciumion bindet dabei an vier THF-Moleküle (mittl. Ca-O 234,0 pm) und den verbrückenden Carbonylliganden des Komplexanions $\{Fe_2(CO)_6(\mu\text{-}CO)(\mu\text{-}PPh_2)\}^-$ (Ca-O 229,8(4) pm, Fe-Fe 257,9(2) pm).



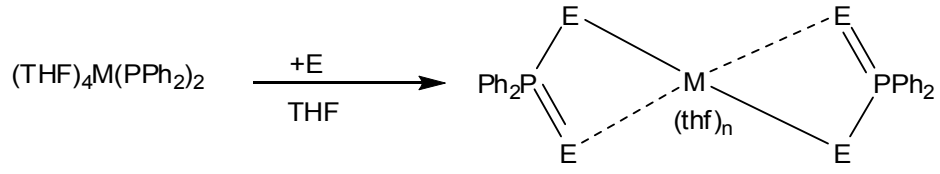
14

Weiterhin stand die Synthese und Charakterisierung von $[(THF)_2Ca\{RNC(PPh_2)NR\}_2]$ im Blickpunkt des Interesses. Setzt man $[(THF)_4Ca(PPh_2)_2]$ (**8**) mit Diisopropyl- oder Dicyclohexylcarbodiimid um, so erhält man die Phospha(III)guanidinate $[(THF)_2Ca\{RNC(PPh_2)NR\}_2]$ (R=isopropyl (**15**) und cyclohexyl (**16**)). Ebenso erlaubt die Metathese von $K\{RNC(PPh_2)NR\}$ mit wasserfreiem CaI_2 die Darstellung der Phospha(III)guanidinate **15** und **16**. Während **15** als *cis*-Isomer erhalten wird, erhält man **16** als *trans*-Isomer. Beide Phospha(III)guanidinate fungieren als zweizähnige Chelatbasen mit einem mittleren Ca-N Abstand von 242,5 pm. Die sehr lange C-P Bindungslänge zwischen dem PPh_2-Fragment und der 1,3-Diazaallyl-Einheit beträgt 190,0 pm. Die Komplexe **15** und **16** zeigen nur eine moderate katalytische Aktivität hinsichtlich der Hydrophosphanylierung von Dialkylcarbodiimiden mit Diphenylphosphan.



15 (R = *i*Pr), **16** (R = Cy)

Die Reaktion von Calcium oder Strontiumdiphenylphosphaniden mit vier Äquivalenten elementaren Schwefels oder grauem Selen in THF ergab die Oxidationsprodukte Calcium- und Strontiumdiphenylphosphinat $(THF)_3Ca[S_2PPh_2]_2$ **17**, $(THF)_3Sr[S_2PPh_2]_2$ **18**, $(THF)_2Ca[Se_2PPh_2]_2$ **19** und $(THF)_3Sr[Se_2PPh_2]_2$ **20**. Sämtliche Komplexe **17-20** wurden als farblose luftstabile Verbindungen kristallisiert. Die Untersuchung der Festkörperstrukturen von **19** und **20** zeigen monomere Verbindungen mit sechsfach koordinierten Calciumionen und siebenfach koordinierten Strontiumionen, welche symmetrisch von Phosphinatliganden umgeben sind. Eine Absättigung der Koordinationssphäre erfolgt durch zwei oder drei THF-Moleküle. In den Festkörperstrukturen der Verbindungen **17** und **18** beobachtet man ebenfalls Monomere mit der Koordinationszahl sieben für Calcium und Strontium. Die Struktur von $M(S_2PPh_2)(THF)_3$ (M = Ca, Sr) kann, hinsichtlich der Koordinationssphäre der Erdalkaliionen, als verzerrte pentagonale Bipyramide beschrieben werden. Betrachtet man die jeweiligen Erdalkalimetall-Schwefelabstände (Ca-S, Sr-S) so stellt man fest, dass sie innerhalb der jeweiligen Verbindung nahezu gleich sind. Der Dithiophosphinatligand kann daher als isobidentate (symmetrische) Chelatbase aufgefasst werden, welche einen Vierringchelatkomplex bildet. In beiden Komplexen ist das Phosphoratom verzerrt tetraedrisch umgeben und weist S-P-S Bindungswinkel von 113,82(5)° und 114,37(5)° sowie 115,31(12)° und 115,97(3)° auf.



M =	E =
Ca	S, n = 3 (**17**)
Sr	S, n = 3 (**18**)
Ca	Se, n = 2 (**19**)
Sr	Se, n = 3 (**20**)

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A Crystallographic Data

The intensity data for the compounds were collected on a Nonius KappaCCD diffractometer using graphite-monochromated Mo-K_α radiation. Data were corrected for Lorentz and polarization effects but not for absorption effects [216, 217]. The structures were solved by direct methods (SHELXS) [218] and refined by full-matrix least squares techniques against F_o^2 (SHELXL-97) [219]. The hydrogen atoms were included at calculated positions with fixed thermal parameters. All non-hydrogen and non-disordered atoms were refined anisotropically [219]. XP (SIEMENS Analytical X-ray Instruments, Inc.) was used for structure representations.

Table 1: Crystal data and refinement details for the X-ray structure determinations of **10a, 10b, 10c** and **10d**.

Compound	**10a**	**10b**	**10c**	**140d**
formula	$C_{30}H_{28}P_2$	$C_{40}H_{32}P_2$	$C_{34}H_{40}P_2Si_2$	$C_{46}H_{44}P_2$
fw ($g \cdot mol^{-1}$)	450.46	574.60	566.78	658.75
T/°C	-90 (2)	-90 (2)	-90 (2)	-90 (2)
crystal system	tetragonal	triclinic	monoclinic	triclinic
space group	$I4_1/2$	$P\bar{1}$	$P2_1/c$	$P\bar{1}$
a/ Å	24.0265(12)	8.072(3)	12.2046(7)	9.8621(5)
b/ Å	24.0265(12)	9.618(3)	11.1734(5)	12.5438(4)
c/ Å	8.4030(5)	11.254(2)	11.8562(5)	16.5100(5)
α/°	90.00	72.161(17)	90.00	109 .259(2)
β/°	90.00	87.168(17)	96.367(3)	93.233(2)
γ/°	90.00	66.612(10)	90.00	103.269(2)
V/Å^3	4850.8(4)	760.8(4)	1606.79(14)	1857.15(12)
Z	8	1	2	2
ρ ($g \cdot cm^{-3}$)	1.234	1.254	1.171	1.178
μ (cm^{-1})	1.95	1.71	2.31	1.84
measured data	15324	5072	9716	13566
data with I > 2σ(I)	2772	3349	3615	8451
unique data / R_{int}	1828	1434	2966	5214
wR_2 (all data, on F^2)[a)]	0.1114	0.2277	0.1179	0.1367
R_1 ($I > 2\sigma(I)$)[a)]	0.0476	0.0911	0.0450	0.0521
s[b)]	1.005	1.014	1.014	1.004
Res. dens./$e \cdot Å^{-3}$	0.253/-0.216	0.984/-0.332	1.248/-0.264	0.320/-0.298
CCDC No.		693498		

[a)] $R_1 = (\Sigma \,||F_o| - |F_c||)/\Sigma|F_o|$, $wR_2 = \{\Sigma[w(F_o^2-F_c^2)^2]/\Sigma[w(F_o^2)^2]\}^{1/2}$, $w^{-1} = \sigma^2(F_o^2) + (aP)^2$.

[b)] $s = \{\Sigma[w(F_o^2-F_c^2)^2]/(N_o-N_p)\}^{1/2}$.

Table 2: Crystal data and refinement details for the X-ray structure determinations of **13a**, **13b** and **13c**.

Compound	**13a**	**13b**	**13c**
formula	$C_{32}H_{32}Cl_4O_2P_2$	$C_{41}H_{36}O_3P_2$	$C_{34}H_{40}O_2P_2Si_2$
fw ($g \cdot mol^{-1}$)	652.32	638.64	598.78
T/°C	-90 (2)	-90 (2)	-90 (2)
crystal system	monoclinic	monoclinic	monoclinic
space group	$P2_1/n$	$P2_1/c$	$P2_1/n$
a/ Å	8.5553(4)	19.0990(5)	9.091(4)
b/ Å	16.2259(8)	9.3722(3)	11.0230(4)
c/ Å	12.3938(3)	19.099(5)	16.4554(7)
α/°	90.00	90.00	90.00
β/°	109.850(2)	104.750(2)	100.455(2)
γ/°	90.00	90.00	90.00
V/Å^3	1618.25(2)	3306.09(16)	1606.79(14)
Z	2	4	2
ρ ($g \cdot cm^{-3}$)	1.339	1.283	1.226
μ (cm^{-1})	4.93	1.71	2.37
measured data	11284	21777	10995
data with I > 2σ(I)	3680	7513	3721
unique data / R_{int}	2909	5054	2580
wR_2 (all data, on F^2)[a)]	0.2013	0.1548	0.1120
R_1 ($I > 2\sigma(I)$)[a)]	0.0682	0.0557	0.0421
s[b)]	1.006	1.015	0.960
Res. dens./$e \cdot Å^{-3}$	0.885/-0.858	0.595/-0.577	0.242/-0.366
CCDC No.			

[a)] $R_1 = (\Sigma \,||F_o| - |F_c||)/\Sigma |F_o|$, $wR_2 = \{\Sigma[w(F_o^2-F_c^2)^2]/\Sigma[w(F_o^2)^2]\}^{1/2}$, $w^{-1} = \sigma^2(F_o^2) + (aP)^2$.

[b)] $s = \{\Sigma[w(F_o^2-F_c^2)^2]/(N_o-N_p)\}^{1/2}$.

Table 3: Crystal data and refinement details for the X-ray structure determinations of **9a** and **12**.

Compound	**9a**	**12**
formula	$C_{21}H_{19}P$	$C_{36}H_{40}P_2$
fw ($g \cdot mol^{-1}$)	302.33	534.62
T/°C	-90 (2)	-90 (2)
crystal system	monoclinic	triclinic
space group	$P2_1/c$	$P\bar{1}$
a/ Å	5.9484(3)	10.0187(8)
b/ Å	17.9623(8)	10.2630(8)
c/ Å	15.4154(8)	15.6487(9)
α/°	90.00	91.435(4)
β/°	94.111(3)	106.188(4)
γ/°	90.00	99.927(4)
V/Å^3	1642.85(14)	1517.55(19)
Z	4	2
ρ ($g \cdot cm^{-3}$)	1.222	1.170
μ (cm^{-1})	1.62	1.66
measured data	10775	10446
data with I > 2σ(I)	3744	6793
unique data / R_{int}	2743	4006
wR_2 (all data, on F^2)[a)]	0.1088	0.1202
R_1 ($I > 2\sigma(I)$)[a)]	0.0406	0.0533
s[b)]	1.003	0.984
Res. dens./e·Å^{-3}	0.210/-0.350	0.237/-0.244
CCDC No.		

[a)] $R_1 = (\Sigma \,||F_o| - |F_c||)/\Sigma|F_o|$, $wR_2 = \{\Sigma[w(F_o^2-F_c^2)^2]/\Sigma[w(F_o^2)^2]\}^{1/2}$, $w^{-1} = \sigma^2(F_o^2) + (aP)^2$.

[b)] $s = \{\Sigma[w(F_o^2-F_c^2)^2]/(N_o-N_p)\}^{1/2}$.

Table 4: Crystal data and refinement details for the X-ray structure determinations of the contact ion pair $[(thf)_4Ca\{Fe_2(CO)_6(\mu\text{-}CO)(\mu\text{-}PPh_2)\}_2]$ (**14**).

Compound	**14**
formula	$C_{54}H_{52}CaFe_4O_{18}P_2$
fw ($g \cdot mol^{-1}$)	1314.38
T/°C	-90(2)
crystal system	trilinic
space group	Pī
a/ Å	10.097(2)
b/ Å	11.905(2)
c/ Å	13.314(3)
α/°	101.07(3)
β/°	95.11(3)
γ/°	109.51(3)
V/Å^3	1460.0(6)
Z	1
ρ ($g \cdot cm^{-3}$)	1.495
μ (cm^{-1})	11.86
measured data	9765
parameters	353
data with I > 2σ(I)	3490
unique data / R_{int}	6492/0.0491
wR_2 (all data, on F^2)[a)]	0.1694
R_1 ($I > 2\sigma(I)$)[a)]	0.0723
s[b)]	1.019
Res. dens./$e \cdot Å^{-3}$	0.441/-0.424
CCDC No.	720836

[a)] $R_1 = (\Sigma \,||F_o| - |F_c||)/\Sigma|F_o|$, $wR_2 = \{\Sigma[w(F_o^2-F_c^2)^2]/\Sigma[w(F_o^2)^2]\}^{1/2}$, $w^{-1} = \sigma^2(F_o^2) + (aP)^2$.

[b)] $s = \{\Sigma[w(F_o^2-F_c^2)^2]/(N_o-N_p)\}^{1/2}$.

Table 5: Crystal data and refinement details for the X-ray structure determinations of **15** and **16**.

Compound	**15**	**16**
formula	$C_{46}H_{64}CaN_4O_2P_2$ * 0.25 C_4H_8O	$C_{58}H_{80}CaN_4O_2P_2$
fw ($g \cdot mol^{-1}$)	825.06	967.28
T/°C	20(2)	-90(2)
crystal system	monoclinic	monoclinic
space group	C2/c	$P2_1/c$
a/ Å	49.7397(12)	13.9698(4)
b/ Å	10.1289(2)	16.0913(6)
c/ Å	20.0391(3)	12.9972(5)
α/°	90	90
β/°	105.916(1)	114.195(2)
γ/°	90	90
V/Å^3	9708.8(3)	2665.02(16)
Z	8	2
ρ ($g \cdot cm^{-3}$)	1.129	1.205
μ (cm^{-1})	2.34	2.23
measured data	46543	18585
data with I > 2σ(I)	7297	3960
unique data / R_{int}	11095/0.0706	6083/0.0651
wR_2 (all data, on F^2)[a)]	0.1630	0.1082
R_1 ($I > 2\sigma(I)$)[a)]	0.0562	0.0454
s[b)]	1.028	1.015
Res. dens./$e \cdot Å^{-3}$	0.366/-0.387	0.273/-0.292
CCDC No.	723058	723059

[a)] $R_1 = (\Sigma \,||F_o| - |F_c||)/\Sigma|F_o|$, $wR_2 = \{\Sigma[w(F_o^2-F_c^2)^2]/\Sigma[w(F_o^2)^2]\}^{1/2}$, $w^{-1} = \sigma^2(F_o^2) + (aP)^2$.

[b)] $s = \{\Sigma[w(F_o^2-F_c^2)^2]/(N_o-N_p)\}^{1/2}$.

Table 6: Crystal data and refinement details for the X-ray structure determinations of **17**, **18, 19** and **20**.

Compound	**17**	**18**	**19**	**20**
formula	$C_{36}H_{42}CaO_3P_2S_4$	$C_{36}H_{44}CaO_3P_2S_4$	$C_{36}H_{36}CaO_2P_2Se_4$	$C_{36}H_{44}CaO_3P_2Se_4$
fw ($g \cdot mol^{-1}$)	752.96	802.51	870.47	990.11
T/°C	-90 (2)	-90 (2)	-90 (2)	-90 (2)
crystal system	monoclinic	monoclinic	monoclinic	monoclinic
space group	$P2_1/c$	$P2_1$	$P2_1$	$P2_1/n$
a/ Å	9.8382(8)	15.7762(4)	8.8990(18)	17.2391(3)
b/ Å	19.967(2)	13.1205(5)	26.290(5)	32.1960(4)
c/ Å	10.9869(13)	20.0254(6)	15.472(3)	21.9626(4)
α/°	90.00	90.00	90.00	90.00
β/°	95.765(7)	108.406(2)	103.45(3)	102.443(1)
γ/°	90.00	90.00	90.00	90.00
V/Å^3	1932.3(4)	3933.0(2)	3520.5(12)	11903.6(3)
Z	2	4	4	12
ρ ($g \cdot cm^{-3}$)	1.286	1.355	1.642	1.657
μ (cm^{-1})	4.91	16.97	44.32	51.41
measured data	25959	28266	19545	71584
data with I > 2σ(I)	8806	16924	13134	26636
unique data / R_{int}	5751	10287	10683	13934
wR_2 (all data, on F^2)[a)]	0.1381	0.1444	0.0879	0.1126
R_1 ($I > 2\sigma(I)$)[a)]	0.0522	0.0629	0.0405	0.0573
s[b)]	1.018	0.998	1.012	0.948
Res. dens./$e \cdot Å^{-3}$	0.690/-0.385	0.660/-0.492	0.429/-0.591	1.302/-0.876
CCDC No.				

[a)] $R_1 = (\Sigma \,||F_o| - |F_c||)/\Sigma|F_o|$, $wR_2 = \{\Sigma[w(F_o^2-F_c^2)^2]/\Sigma[w(F_o^2)^2]\}^{1/2}$, $w^{-1} = \sigma^2(F_o^2) + (aP)^2$.

[b)] $s = \{\Sigma[w(F_o^2-F_c^2)^2]/(N_o-N_p)\}^{1/2}$.

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Declaration of Originality

I certify that the work presented here is, to the best of my knowledge and belief, original and the result of my own investigations, except as acknowledged, and has not been submitted, either in part or whole, for a degree at this or any other university.

Ich erkläre, dass ich die vorliegende Arbeit selbstständig und nur unter Verwendung der angegebenen Hilfsmittel, persönlichen Mitteilungen und Quellen angefertigt habe und dass ich nicht die gleiche, eine in wesentlichen Teilen ähnliche oder eine andere Abhandlung bei einer anderen Hochschule als Dissertation eingereicht habe.

Tareq Al-Shboul Jena, den 22.02.2010

List of Publications

1- Al-Shboul, **Tareq M. A.;** Goerls, Helmar; Westerhausen, Matthias. Calcium-mediated hydrophosphination of diphenylethyne and diphenylbutadiyne as well as crystal structure of 1,4-diphenyl-1,4-bis(diphenylphosphanyl)buta-1,3-diene. Inorganic Chemistry Communications (**2008**), 11(12), 1419-1421.

2- Al-Shboul, **Tareq Mousa Ali**; Goerls, Helmar; Westerhausen, Matthias. Synthesis and X-ray crystal structure of $[(thf)_4Ca\{Fe_2(CO)_6(\mu\text{-}CO)(\mu\text{-}PPh_2)\}_2]$. Jordan Journal of Chemistry (**2009**), 4(2), 111-118.

3- Al-Shboul, **Tareq M. A**.; Gritt Volland, Helmar Görls, Matthias Westerhausen. [Bis(tetrahydrofuran-*O*)-bis(1,3-dialkyl-2-diphenylphosphanyl-1,3-diazaallyl)calcium] - Synthesis and Crystal Structures of Calcium Bis[phospha(III)guanidinates] and Investigations of Catalytic Activity**.** Z. Anorg. Allg. Chem. (**2009**) , 635 , 1568-1572 .

4- Katja Wimmer, Christin Birg, Robert Kretschmer, **Tareq M. A. Al-Shboul**, Helmar Görls, Sven Krieck, Matthias Westerhausen. Novel Synthetic Routes to s-Block Metal 2,5-Diphenylphospholides and Crystal Structures of the Bis(tetrahydrofuran) Complexes of the Potassium, Calcium, and Strontium Derivatives. Zeitschrift für Naturforschung B.(**2009**), 64b, 1360-1368.