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Catalytic synthesis of vinylphosphanes *via* calcium-mediated intermolecular hydrophosphanylation of alkynes and butadiynes

Tareq M.A. Al-Shboul [a], Villö K. Pálfi [b], Lian Yu [b], Robert Kretschmer [a], Katja Wimmer [a], Reinald Fischer [a], Helmar Görls [a], Markus Reiher [b,*], Matthias Westerhausen [a,**]

[a] Institut für Anorganische und Analytische Chemie, Friedrich-Schiller-Universität Jena August-Bebel-Str. 2, D-07743 Jena, Germany
[b] Laboratorium für Physikalische Chemie, ETH Zurich, Hönggerberg Campus, Wolfgang-Pauli-Str. 10, CH-8093 Zurich, Switzerland

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ABSTRACT

The calcium complex $[(thf)_4Ca(PPh_2)_2]$ (**1**) is a very effective catalyst for the hydrophosphanylation of substituted alkynes of the type R–C≡C–R (R = Me, Ph) yielding (*E*)-1,2-diphenyl-1-diphenylphosphanylethene (**2a**) and (*Z*)-1-phenyl-2-diphenylphosphanyl-1-propene (**2b**). The calcium-mediated hydrophosphanylation of butadiynes of the type R–C≡C–C≡C-R (R = Me, $SiMe_3$, Ph, Mes, *t*Bu) proceeds less selectively and diverse products are obtained such as 1,4-substituted 1,4-bis(diphenylphosphanyl)-1,3-butadienes (**3**), 1,4-diphenyl-1,2-bis(diphenylphosphanyl)-1,3-butadiene (**4**), and 1,4-di(tert-butyl)-1,4-bis(diphenylphosphanyl)buta-1,2-diene (**5**). Besides these regioisomers also several configuration isomers with respect to the C=C double bonds [(*E*)/(*Z*) isomerism] are obtained. A catalytic cycle can be formulated with the first addition of a Ca–P bond of the catalyst **1** to a C≡C triple bond always leading to the formation of an intermediate with the newly formed C–P bond in 1-position whereas the remaining phosphanido calcium fragment binds to the carbon in 2-position. The addition of a second diphenylphosphane is much faster and therefore, only two-fold hydrophosphanylated butadiynes are observed. Neither addition products with only one $HPPh_2$ group nor those with more than two PPh_2 substituents are obtained.

1. Introduction

Bidentate 1,4-bis(diorganylphosphanyl)butadienes play an important role as ligands at catalytically active metal centers. Especially important proved to be the ligand class of 1,4-bis(diphenylphosphanyl)-1,3-butadienes (NUPHOS) which were prepared firstly by Doherty et al. [1,2] *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 $ClPPh_2$. Thus far, 1,2,3,4-tetramethyl- and 1,2,3,4-tetraphenyl-NUPHOS were applied as ligands in catalytically active metal complexes. Comparisons with other well-established ligands such as 2,2′-bis(diphenylphosphanyl)-1,1′-binaphthyl (BINAP) [3,4] and 2,2′-bis(diphenylphosphanyl) biphenyl (BIPHEP) [5,6] showed the advantages of these conformationally more flexible NUPHOS ligands. Diphenyl-vinylphosphanes can also be reductively coupled by e.g. lithium yielding 1,4-bis (diphenylphosphanyl)butanes with a saturated carbon backbone [7]. In addition, the reduction of 1,4-bis(diphenylphosphanyl)-1,4-diphenyl-1,3-butadienes with potassium leads to cleavage of the $P–C_{Ph}$ bonds and the formation of potassium 2,5-diphenylphospholides [8]; metathetical exchange of K^+ *via* the reaction of this phospholide with CaI_2 in THF yields bis(tetrahydrofuran)calcium bis (2,5-diphenylphospholide).

Catalytic hydrophosphanylation of butadiynes with diphenylphosphane offers the possibility to prepare 1,4-disubstituted NUPHOS ligands. Hydrophosphanylation can be performed successfully with many transition metal-based catalysts [9] and sometimes even metal-free [10]. Common metals in hydrophosphanylation reactions of alkynes or butadiynes are transition metals such as cobalt, copper, nickel, palladium, rhodium, ruthenium, yttrium, zirconium, as well as lanthanoids such as lanthanum, samarium, ytterbium, and others. Substitution of these – often expensive – noble transition metals and lanthanoids by calcium would allow a more economic catalysis, even though lower turnover 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 [11,12] does not involve a change of the

* Corresponding author. Fax: +41 44 633 15 94.
** Corresponding author. Fax: +49 3641 948102.
E-mail addresses: markus.reiher@phys.chem.ethz.ch (M. Reiher), m.we@uni-jena.de (M. Westerhausen).

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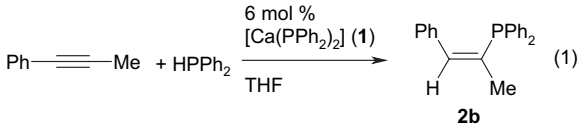
oxidation state of Yb(II) and a similar reaction behaviour of calcium (II) and ytterbium(II) compounds seems possible. Catalytic activity requires easily accessible vacant coordination sites for substrate binding. This prerequisite can be achieved by bulky groups at the periphery of the molecule in order 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 $[(thf)_4Ca(PPh_2)_2]$ (**1**) with potentially labile THF ligands. The bis(diphenylphosphanido) complexes of calcium are easily accessible, monomeric in solution and in the solid state [13,14], and soluble in common organic solvents and, hence, are possible catalysts for hydrophosphanylation reactions. Contrary to this behaviour, monophenylphosphanides of the alkaline earth metals are oligomeric or polymeric in solution and in the solid state and show poor solubility in common organic solvents [15].

Organocalcium chemistry represents a vastly developing branch of organometallic chemistry for many reasons [16–18]. Uncommon structures of organocalcium derivatives such as bent molecules $(Ca[C(SiMe_3)_3]_2)$ [19] or pyramidal calciates ($[Ca\{CH(SiMe_3)_2\}_3]^-$) [20] sparked interest in this compound class and beyond that in compounds of d^0 metals in general [21]. 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 typical *s*-block elements but also as early transition metals. 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 [22]. Calcium-mediated hydroamination reactions were already investigated [23–26] as well as hydrosilylation of alkenes with benzylcalcium derivatives [26,27]. Furthermore, calcium-mediated hydrophosphanylations of alkenes and diphenylacetylene [28] succeeded with sterically encumbered calcium complexes whereas the hydrophosphanylation of carbodiimides [29] was also catalyzed by alkaline earth metal bis[bis(trimethylsilyl)amides] of Ca, Sr, and Ba. 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. Crimmin et al. [30] and Zuyls et al. [31] also studied the dimerization of aldehydes to carboxylic esters (Tishchenko reaction) employing calcium-based catalysts. Very recently, even catalytic hydrogenation of alkenes such as 1,1-diphenylethene succeeded with diketiminatocalcium hydride complexes [32]. Even classic organic reactions such as Michael, Aldol and Mannich reactions can be catalyzed by alkoxides of the heavy alkaline earth metals [33]. The use of calcium in catalyst systems tremendously gained on importance with the availability of soluble organocalcium complexes. We already tested the effectivity of $[(thf)_4Ca(PPh_2)_2]$ (**1**) as a catalyst for stereoselective hydrophosphanylation of diphenylbutadiyne with diphenylphosphane [34]. Now we extend our investigations on butadiynes with different substituents such as alkyl, aryl and trialkylsilyl in order to investigate the scope of this heterofunctionalization of these alkynes.

2. Results and discussion

2.1. Synthesis and catalysis

A calcium complex (20 mol %) with a bulky *N,N′*-diaryl-β-diketiminato ligand catalyzed the hydrophosphanylation of 1,2-diphenylethyne and a nearly quantitative conversion was achieved after 13 h at 75 °C in THF [28]. In less than two hours *trans*-1,2-diphenyl-1-diphenylphosphanylethene (**2a**) formed quantitatively at room temperature in a similar reaction with catalytic amounts of $[(thf)_4Ca(PPh_2)_2]$ (**1**) (6 mol %). The hydrophosphanylation of 1-phenylprop-1-yne according to Eq. (1) proceeded regio- and stereoselectively and yielded (*Z*)-1-phenyl-2-diphenylphosphanyl-1-propene (**2b**). Vinylphosphanes are not repeatedly phosphanylated by another equivalent of $HPPh_2$.



These vinylphosphanes are well-known substances and a comparison of the NMR parameters verified the formation of **2a** [35] and **2b** [36,37]. The molecular structures of the (*Z*)- and (*E*)-isomers of **2a** show distortions of the bond angles as expected for sterically strained alkenes [37]. Molecular structure and numbering scheme of **2b** is shown in Fig. 1. Selected structural parameters are compared in Table 1 with literature values [37] of *cis*- and *trans*-1,2-diphenyl-1-diphenylphosphanylethene (**2a**) and of *cis*-1-phenyl-2-diphenylphosphanylethene (**A**) [38]. In **2b** 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 **A**) leads to an extremely large P1–C1–C2 angle of more than 130° suggesting that the methyl group in **2b** 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.

Hydrophosphanylation of butadiynes can in principle yield a variety of isomers with respect to their constitution and configuration, depending on the reaction mechanism. In Scheme 1 the constitution isomers of resulting 1,3- as well as 1,2-butadienes

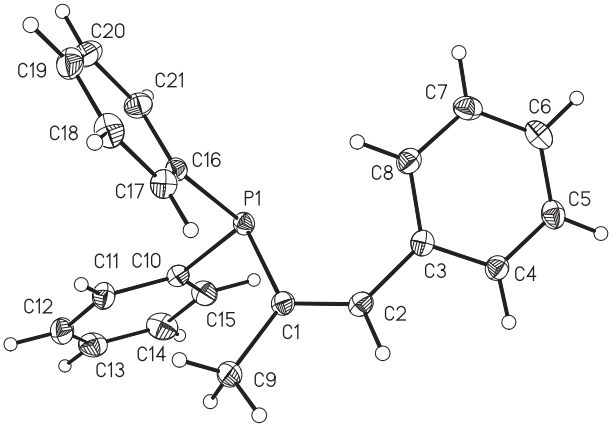


Fig. 1. Molecular structure and numbering scheme of *cis*-1-phenyl-2-diphenylphosphanyl-1-propene (**2b**). The ellipsoids represent a probability of 40%, H atoms are drawn with arbitrary radii. Selected structural data are listed in Table 1.

Table 1
Comparison of selected structural data of *cis*- and *trans*-1,2-diphenyl-1-diphenylphosphanylethene (**2a**) [36], *cis*-1-phenyl-2-diphenylphosphanylethene (**A**) [34], and *cis*-1-phenyl-2-diphenylphosphanyl-1-propene (**2b**).

	(*Z*)-**2a**	(*E*)-**2a**	(*Z*)-***A***	(*Z*)-**2b**
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)

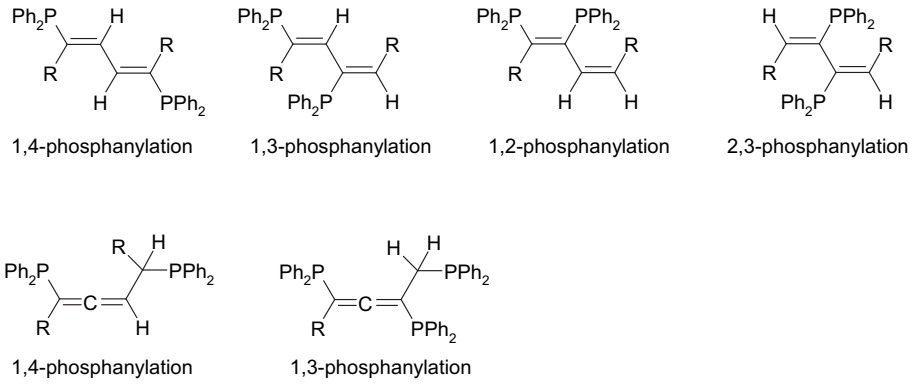
(allenes) are summarized. Isomers which would result from hydrophosphanylation of C═C double bonds are excluded because such a reaction was not observed for vinylphosphanes.

A general procedure for the hydrophosphanylation of butadiynes in order to investigate the hydrophosphanylation in dependency of the substituent R was applied. The butadiyne was dissolved in THF and cooled to −78 °C. Then diphenylphosphane and approximately 5 mol-% of the catalyst [$(thf)_4Ca(PPh_2)_2$] (**1**) were added. Under these conditions addition of $HPPh_2$ to the butadiynes occurred yielding a variety of products. The major components were different isomers of the 1,4-bis(diphenylphosphanyl)-1,3-butadienes (**3**) via an addition of the P–H bond to the C≡C triple bonds. Substituents such as methyl, phenyl, 2,4,6-trimethylphenyl (mesityl), and trimethylsilyl are tolerated at the butadiyne. In a fast reaction, different configuration isomers of 1,4-bis(diphenylphosphanyl)-1,3-butadienes **3** (NUPHOS) were formed with good yields. These isomers are shown in Scheme 2. However, the ^{31}P NMR spectra also showed additional resonances of small intensities in the same region. Despite the diversity of observed isomers at least one diphenylphosphanyl group was bound geminally to the substituent R regardless of its inductive and mesomeric effects. Furthermore, 2,3-bis(diphenylphosphanyl)-1,3-butadienes with both phosphanyl groups in vicinal positions to R were not observed. Steric and electronic reasons are responsible for this finding. The 1-position is sterically more shielded than the position vicinal to R and therefore the PPh_2 unit binds geminally to R whereas the very bulky $Ca(thf)_4PPh_2$ fragment coordinated to the 2-position. In addition, the negative charge can only be delocalized effectively if calcium binds to the 2-position whereas a calcium-carbon bond to the 1-position does not allow such a charge delocalization. Similar reasons are valid for the second hydrophosphanylation and therefore also 1,3-bis(diphenylphosphanyl)-1,3-butadienes are rather unlikely to form.

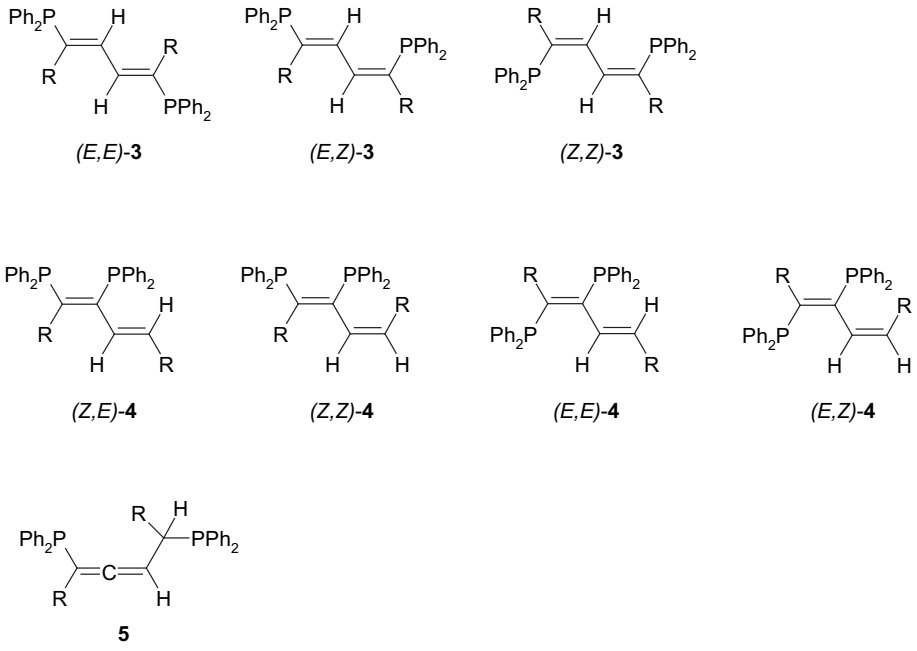
In order to clarify the product distribution single crystals were grown and the crystal structures were determined. From the ^{31}P NMR spectra of the product mixtures and of the single crystals an unambiguous assignment of the resonances was possible. A comparison of this data is given in Table 2. In general the resonances of the phosphanyl group at an alkene moiety with a (*Z*)-configuration lies at higher field than the phosphanyl substituent of an (*E*)-isomer. For the methyl and mesityl derivatives only the (*E,E*)-, (*E,Z*)-, and (*Z,Z*)-isomers were observed with relative ratios of 1:2:1 (R = Me) and 5:1:5 (R = Mes). The calcium-mediated hydrophosphanylation of 2,2,7,7-tetramethylocta-3,5-diyne [di(tert-butyl)butadiyne] gave another major compound, namely the allene derivative 2,2,7,7-tetramethyl-3,6-bis(diphenylphosphanyl)octa-3,4-diene (**5**) which contains a chiral carbon atom and axial chirality. The yttrium-mediated hydrophosphanylation [39] and ytterbium-mediated hydrophosphanylation [40–42] of butadiynes also leads to the formation of 1,3-butadienes and buta-1,2-dienes depending on the substituent at the employed butadiyne. The largest number of different products was obtained for the hydrophosphanylation of diphenylbutadiyne. Besides the isomers of **3** also 1,4-diphenyl-1,2-bis(diphenylphosphanyl)-1,3-butadiene (**4**) was found and characterized by X-ray structure determination. Depending on the substituent R the product ratios and also the number of products varies. A statistical product mixture was observed for R = Me, whereas the bulkier mesityl group disfavours the mixed (*E,Z*)-isomer of **3**. Due to the fact that the formation of tetraphenyldiphosphane plays no role a radical mechanism can be excluded.

From these findings several key features must be explained:

(i) The product distribution strongly depends on the nature of the substituents of the butadiyne. The bulkiness of this group seems to be more important than the electronic properties.
(ii) One diphenylphosphanyl group is always bound at C1 excluding isomers such as 1,4-diorganyl-2,3-bis(diphenylphosphanyl)butadiene.
(iii) The second diphenylphosphanyl substituent can either be bound at C2 (leading to **4**) or C4 (yielding **3** or **5**); however, a 1,3-diphenylphosphanyl substituted isomer was not observed.
(iv) Calcium-mediated hydrophosphanylation of C≡C triple bonds is strongly favoured compared to the addition of $HPPh_2$ to alkene functionalities. Therefore, saturated and quadruply hydrophosphanylated butadiynes [yielding 1,4-diorganyl-tetrakis(diphenylphosphanyl)butanes] were not detected.



Scheme 1. Constitution isomers of a twofold hydrophosphanylation of butadiynes yielding 1,3- (upper row) and 1,2-butadienes (bottom row); *E/Z* isomerism is not shown. Products which result from $HPPh_2$ addition to C═C double bonds are excluded.



Scheme 2. Selection of possible products of the calcium-mediated twofold addition of diphenylphosphane to butadiynes; configuration isomers of 1,4-bis(diphenylphosphanyl)-1,3-butadienes (**3**) and of 1,2-bis(diphenylphosphanyl)-1,3-butadienes (**4**) as well as allene **5**. Isomers based on chirality of **5** are not shown.

Taking these observations into account, a reaction sequence as shown in Scheme 3 can be proposed. In solution dissociation of the catalyst complex $[(thf)_4Ca(PPh_2)_2]$ and release of THF molecules lead to formation of free coordination sites at the alkaline earth metal. Thereafter the *cis*-addition of a Ca–P bond to a C≡C bond with the P atom at C1 and the calcium atom at C2 (regardless of the electronic properties of the butadiyne) follows. With this orientation the negative charge of the carbanion can be delocalized over the remaining π-system leading to the isomers in the first column (in the red frame). Due to the fact that the hydrophosphanylation was performed in THF the formation of a solvent-separated ion pair of the type $[(thf)_5CaPPh_2]^+$ $[Ph_2P(R)C{=}C{-}C{\equiv}C{-}R]^-$ represents another option. Protonation of this anion yields the but-1-ene-3-ynes or buta-1,2,3-trienes (allenes) and regains the catalyst $Ca(PPh_2)_2$. The unsaturated molecule will not leave the vicinity of the alkaline earth metal and a second Ca–P addition and another protonation step follow. The ability of alkynes to form adducts with alkaline earth metal complexes was observed earlier [38,43] and explains without restraints that the remaining π-system of this molecule is preferred compared to another butadiyne molecule.

Based on this concept, a catalytic cycle as shown in Fig. 2 can be proposed with the THF molecules being neglected for clarity reasons. The Ca–P bond adds to one of the C≡C triple bonds yielding complex **A** which can isomerize as shown in Scheme 3. A very similar addition reaction was observed earlier for the reaction of $[Mg\{P(SiMe_3)_2\}_2]$ [38] 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 [44]. 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-diorganyl-1-diphenylphosphanyl-1-butene-3-yne (**B**) or 1,4-diorganyl-1-diphenylphosphanyl-1,2,3-butatriene (**C**). Side-on coordination of alkynes to calcium [43] and barium cations [38] 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 in **B** or to the allene moiety in **C**. Again, metallation of another molecule of $HPPh_2$ leads to the catalyst and the final products. Now the catalytic cycle restarts again. The high yields of this hydrophosphanylation process shows that the vinylphosphanes are not able to undergo a further hydrophosphanylation reaction, even though calcium-mediated hydrophosphanylation of alkenes was reported for styrene and isoprene [28].

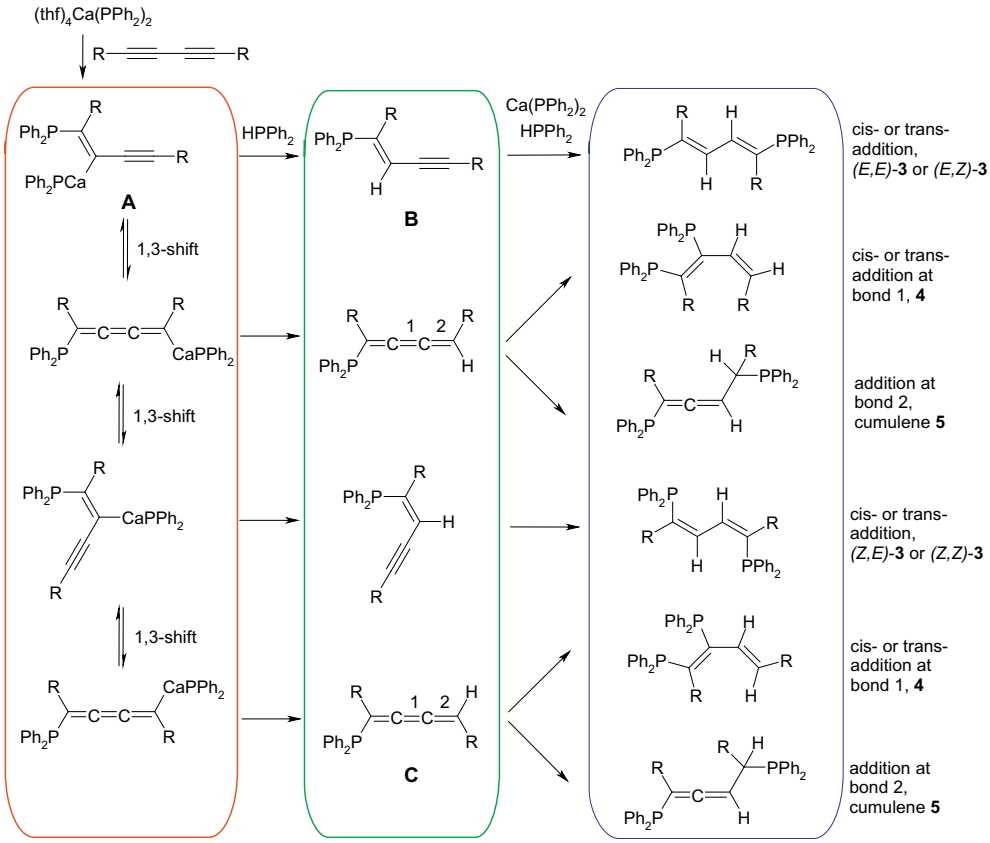
Key values of the hydrophosphanylation of alkynes are summarized in Table 3. The yields refer to isolated crystalline colorless vinylphosphanes after work-up procedures. The calcium-mediated intermolecular hydrophosphanylation proceeds quantitatively within a few minutes as was shown by ^{31}P NMR spectroscopy. The C=C double bonds of the resulting vinylphosphanes are not hydrophosphanylated even in refluxing reaction solutions.

The yields of the calcium-mediated hydrophosphanylation reactions are comparable to those obtained with the ytterbium catalyst. However, the product diversity and distribution seems to depend strongly on reaction conditions. For example, repeated hydrophosphanylation of diphenylbutadiyne gives the 1,4-bis(diphenylphosphanyl)-1,3-butadienes (**3**) as the major products but varying amounts of 1,4-diphenyl-1,2-bis(diphenylphosphanyl)-1,3-butadiene (**4**) were found up to a quarter of all isolated hydrophosphanylation products (see also Table 2).

Table 2
^{31}P NMR parameters and distribution of isomers of 1,4-bis(diphenylphosphanyl)-1,3-butadienes (**3**) after twofold calcium-mediated addition of $HPPh_2$ to butadiynes R–C≡C–C≡C–R. The ^{31}P chemical shifts of compounds which were also characterized by single crystal X-ray diffraction studies are marked by bold numbers.

R	(*E,E*)-**3**	(*E,Z*)-**3**	(*Z,Z*)-**3**	Other resonances
Me	+10.9 (20%)	+9.2/−9.3 (50%)	**−11.0** (30%)	–
Me_3Si	**+5.9** (50%)	+6.1/−4.1 (11%)	−5.6 (23%)	+5.4 (3%), −5.0 (13%)
Ph	**+7.8** (18%)	+7.7/−4.0 (44%)	−5.6 (5%)	**+4.3/−5.5** (23%),[a] +5.3/−2.4 (10%)[b]
Mes	+4.0 (45%)	+3.8/−1.6 (10%)	**−1.6** (45%)	–
*t*Bu	+3.8 (2%)	+2.5/−5.4 (3%)	−5.6 (43%)	**−2.3/−7.1** (52%)[c]

[a] $^3J(P,P) = 196.1$ Hz for compound (*Z,E*)-**4** (see text).
[b] $J(P,P) = 4.1$ Hz.
[c] Allene derivative **5**.



Scheme 3. Reaction pattern of the calcium-mediated hydrophosphanylation of butadiynes (see text). The first step is the *cis*-addition of a Ca–P bond to an alkyne unit followed by 1,3-shift reactions (red frame). Addition of $HPPh_2$ yields the corresponding products in the green frame. Repetition of this reaction sequence allows the synthesis of a variety of isomers of twice hydrophosphanylated butadiynes, a selection is shown in the blue frame.

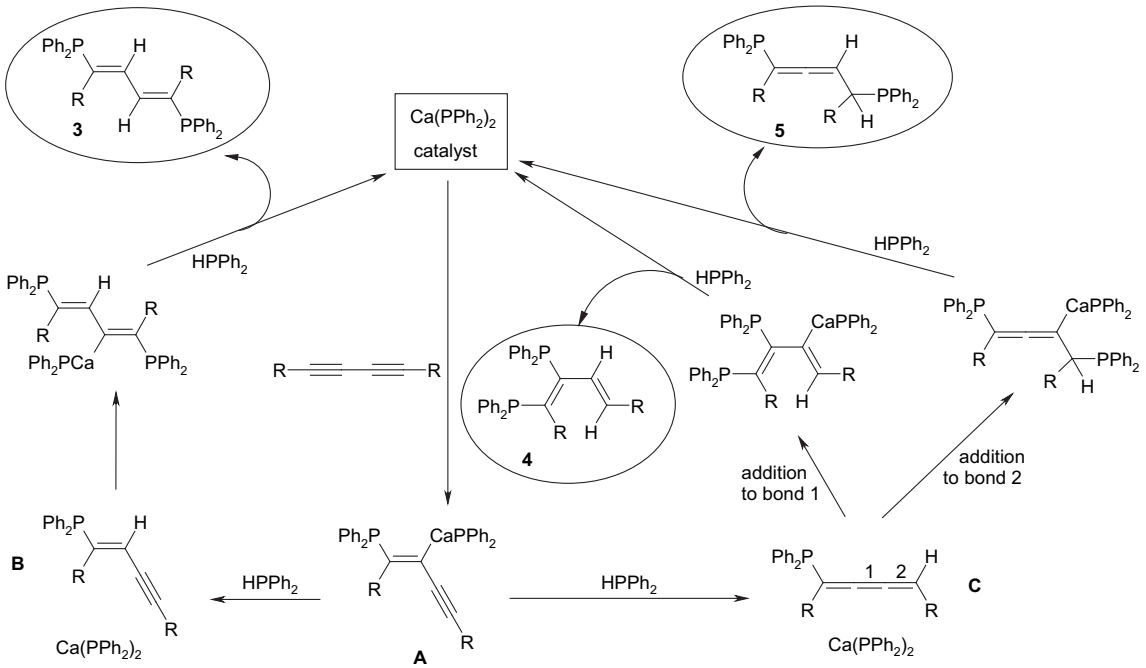


Fig. 2. Catalytic cycle of the hydrophosphanylation of butadiynes with diphenylphosphane in the presence of catalytic amounts of $[(thf)_4Ca(PPh_2)_2]$ (**1**) (shown in a square frame) in THF solution (see text). Neutral thf coligands are neglected for clarity reasons. In addition, only constitution isomers (displayed in ellipsoid frames) are shown in this diagram, conformation (rotamers) and configuration isomersm (*cis*, *trans*) are not shown (see Scheme 2 for this purpose).

Table 3
Reaction conditions and yields of isolated diphenyl-vinylphosphanes obtained via hydrophosphanylation of alkynes and butadiynes in the presence of catalytic amounts of $[(thf)_4Ca(PPh_2)_2]$ **1** in THF solutions.

Product	Employed alkyne	Solvent	Employed cat.	Mol% cat.	Yield[a]	Ref.
2a	Ph–C≡C–Ph	THF	KO*t*Bu	10	26%	[34]
2a	Ph–C≡C–Ph	THF	$LiPPh_2/HNR_2$	[b]	90%	[45]
2a	Ph–C≡C–Ph	THF	$[(thf)_4Ca(PPh_2)_2]$	6	77%	
2a	Ph–C≡C–Ph	CH_3CN	$Pd(PPh_3)_4$	5	95%	[46]
2a	Ph–C≡C–Ph	THF	Yb-catalyst[c]	5	85%	[41]
2a	Ph–C≡C–Ph	C_6D_6	Ca-catalyst[d]	10	94%	[28]
2b	Ph–C≡C–Me	THF	Yb-catalyst[c]	5	80%	[41]
2b	Ph–C≡C–Me	THF	$[(thf)_4Ca(PPh_2)_2]$	5	85%	
3a	Me–C≡C–C≡C–Me	THF	$[(thf)_4Ca(PPh_2)_2]$	5	81%	
3b	Ph–C≡C–C≡C–Ph	THF	$[(thf)_4Ca(PPh_2)_2]$	5	89%	[34]
3c	Me_3Si–C≡C–C≡C–$SiMe_3$	THF	$[(thf)_4Ca(PPh_2)_2]$	5	79%	
3d	Mes–C≡C–C≡C-Mes	THF	$[(thf)_4Ca(PPh_2)_2]$	5	76%	

For comparison reasons, selected examples from the literature are included.
[a] Yield of isolated vinylphosphanes regardless of *cis*- and *trans*-configuration.
[b] No values or details are 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.

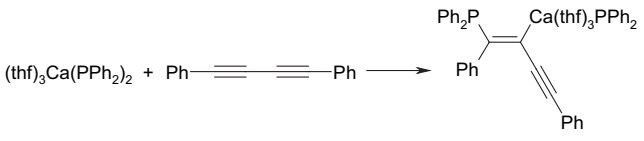
2.2. Quantum chemical investigations

A key feature of the catalytic cycle is the availability of free coordination sites. Therefore, liberation of THF molecules as well as of PPh_2 anions from **1** was determined with the B97-D/RI/TZVPP combination of density functional and basis set. Separation of ions (Eq. (2)) requires a lot of energy ($\Delta E = +306$ kJ mol^{-1}), in contrary to the liberation of a THF ligand (Eq. (3)) ($\Delta E = +25$ kJ mol^{-1}). As the calculations are carried out for isolated (i.e.) unsolvated molecules and not in solution, the ion separation energy is greatly overestimated. However, the liberation energy of a THF ligand can be reliably calculated, and it is rather small. Moreover, the THF molecules cannot solvate negative ions well, and the first solvation layer of THF molecules is already included around the Ca^{2+} ion. Therefore it can be presumed that even in solution the separation of ions is of much higher energy than the liberation of a THF ligand.

$$[(thf)_4Ca(PPh_2)_2] + THF \rightarrow [(thf)_5Ca\text{-}PPh_2]^+ + [PPh_2]^- \quad (2)$$

$$[(thf)_4Ca(PPh_2)_2] \rightarrow [(thf)_3Ca(PPh_2)_2] + THF \quad (3)$$

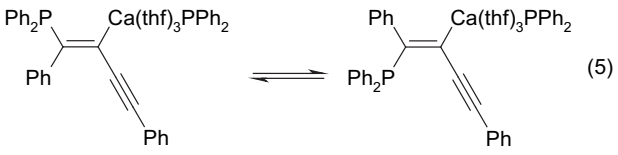
The addition of such an activated calcium complex (only five-fold coordinated) to a C≡C triple bond would be exothermic by $\Delta E = -39$ kJ mol^{-1} (Eq. (4)). This *cis*-addition product is favoured compared to a product with four calcium-bound THF ligands ($\Delta E = +15$ kJ mol^{-1}). This finding can be understood taking into account that hexa-coordinate calcium is favoured with bonds to three THF molecules, a PPh_2 anion (Ca–P 294.6 pm), a carbon atom (Ca–C 260.2 pm), and another phosphorus atom of the newly formed phosphane moiety (Ca–P 311.3 pm). A fourth THF molecule induces steric pressure and leads to an elongation of the calcium–phosphane distance by 100 pm (Ca–P 411.1 pm). The molecular structure of this *Z*-intermediate addition product is displayed in Fig. 3.



(4)

As shown in Scheme 2 the $(thf)_3Ca(PPh_2)$ fragment can undergo a 1,3-shift. The resulting *Z*-1,4-addition product is only +9 kJ mol^{-1} higher in energy and very well accessible under reaction conditions.

Both *E*-isomers of the products of the 1,2-*trans*-addition (see Eq. (5)) and of 1,4-trans-addition reactions are higher in energy by 11 and 13 kJ mol^{-1}, respectively, than the initial *Z*-1,2-addition product shown in Eq. (4). Taking into account the unavoidable method-inherent errors of quantum chemical calculations all these four intermediates have similar energies.



(5)

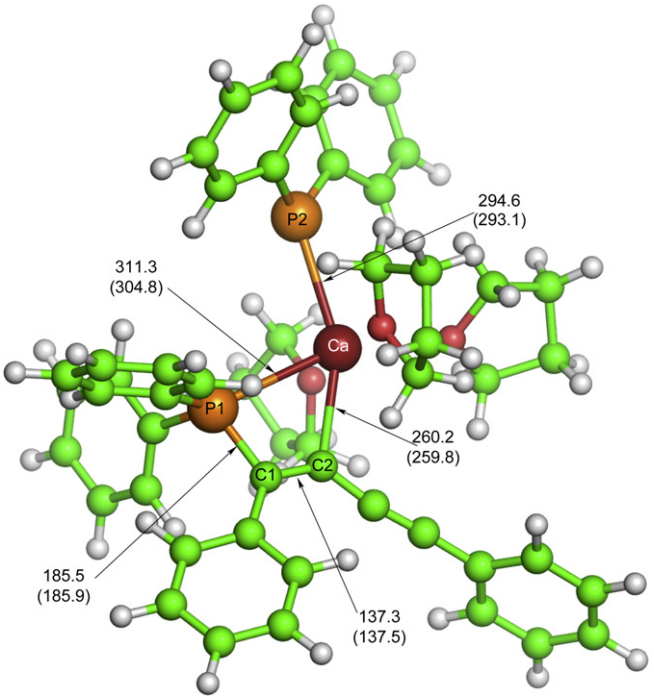
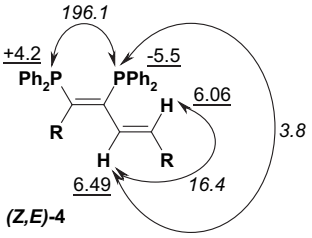


Fig. 3. The B97-D/RI/TZVPP optimized structure of *cis*-1-phosphanido-2-Ca(thf)$_3$PPh$_2$-1,4-diphenyl-buta-1,3-diene (*Z*-intermediate addition product). Selected bond lengths are given in pm (those of the BP86/RI/TZVP optimization are in parantheses).

Table 4
Comparison of the ^{1}H NMR data of the NUPHOS diphosphanes of the type $Ph_2P(R)C{=}CH{-}CH{=}C(R)PPh_2$ **3$_{Me}$** (R = Me), **3$_{Ph}$** (R = Ph), **3$_{Silyl}$** (R = $SiMe_3$), and **3$_{Mes}$** (R = Mes).

	Solvent	$\delta(H_{Vi})$	$^3J(H_{Vi},H_{Vi})$	$^3J(H,P)$	$^4J(H,P)$	$^5J(P,P)$	$\delta(H_{PPh})$	$\delta(H_R)$
(*E,E*)-**3$_{Me}$**	$CDCl_3$	6.50	11.4	12.5	−0.1	0.6	7.1–7.5	1.68 (Me)
(*E,Z*)-**3$_{Me}$**	$CDCl_3$	6.89, 7.02	11.6	4.0, 1.2	<1, <1	<1	7.1–7.5	1.71, 1.72 (Me)
(*Z,Z*)-**3$_{Me}$**	$CDCl_3$	7.66	10.9	20.2	−2.3	<1	7.2–7.4	1.67 (Me)
(*E,E*)-**3$_{Silyl}$**	$CDCl_3$	6.56	12.1	14.2	0.3	<1	7.2–7.4	−0.25 ($SiMe_3$)
(*E,E*)-**3$_{Ph}$**	[D_6]benzene	6.12	11.2	6.5	0.5	<1	7.0–7.3	7.0–7.3(Ph)
(*E,Z*)-**3$_{Ph}$**	[D_6]benzene	6.02, 6.39	16.4	30.0, 3.6	<1, <1	<1	7.0–7.3	7.0–7.3 (Ph)
(*E,E*)-**3$_{Mes}$**[a]	[D_6]benzene	7.57	2.7	13.7	−0.4	<1	7.1–7.4	2.02 (p-Me), 2.10 (o-Me), 6.46 (aryl)
(*Z,Z*)-**3$_{Mes}$**	[D_6]benzene	6.31	11.0	9.2	−0.4	<1	7.1–7.4	1.87 (p-Me), 2.02 (o-Me), 6.60 (aryl)
(*Z,Z*)-**3$_{tBu}$**[a]	$CDCl_3$	7.01	6.0	6.6	−0.5	<1	7.0–7.5	0.93 (*t*Bu)

[a] Assignment is unsecure due to overlap with the resonances of the phenyl groups.



Scheme 4. Chemical shifts δ are shown with underlined numbers, selected coupling constants ^{3}J(H,H), ^{3}J(P,H), and ^{3}J(P,P) are shown in italic.

The isomers with the diphenylphosphanyl groups added in 2-position of the butadiyne are higher in energy by 17 (*cis*-addition, see Eq. (5)) and 25 kJ mol^{-1} (*trans*-addition) than the *cis*-addition product with the phosphanyl group in the 1-position.

2.3. NMR spectroscopy

1,4-Bis(diphenylphosphanyl)-1,3-butadienes (**3**) show characteristic ^{1}H NMR hyperfine structures for the protons of the 1,3-butadiene backbones of an AA′XX′ type (Table 4). The chemical shifts lie at $\delta = 6.2 \pm 0.3$ which is characteristic for vinylic hydrogen atoms. The ^{3}J(H,H) coupling constant shows values around 11.5 ± 0.5 Hz. Larger variation is observed for the ^{3}J(H,P) coupling constants which vary between 6.5 and 17 Hz, however, a correlation between configuration and size of the ^{3}J(H,P) value is not obvious. The remaining ^{4}J(H,P) and ^{5}J(P,P) coupling constants are smaller than 1 Hz.

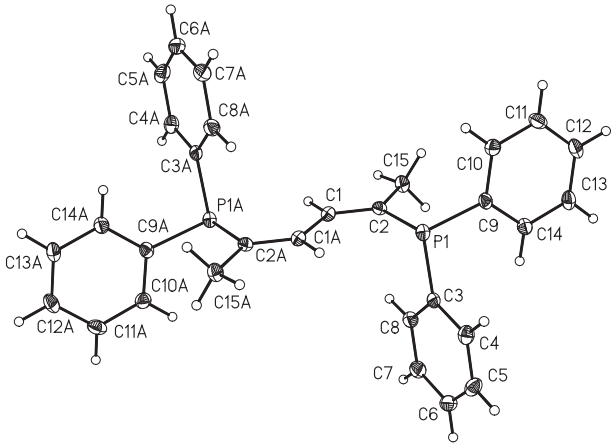


Fig. 4. Molecular structure and numbering scheme of 2,5-bis(diphenylphosphanyl) hexa-2,4-diene [(*Z,Z*)-**3$_{Me}$**]. The ellipsoids represent a probability of 40%, H atoms are drawn with arbitrary radii. Symmetry-related atoms ($-x$, $-y+1$, $-z$) are marked with an "A". Selected structural data are listed in Table 5.

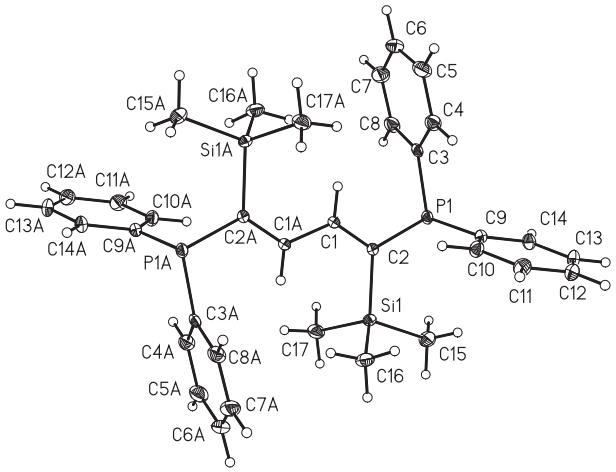


Fig. 5. Molecular structure and numbering scheme of 1,4-bis(trimethylsilyl)-1,4-bis (diphenylphosphanyl)-1,3-butadiene [(*E,E*)-**3$_{Silyl}$**]. The ellipsoids represent a probability of 40%, H atoms are drawn with arbitrary radii. Symmetry-related atoms ($-x+1$, $-y$, $-z+1$) are marked with an "A". Selected structural data are listed in Table 5.

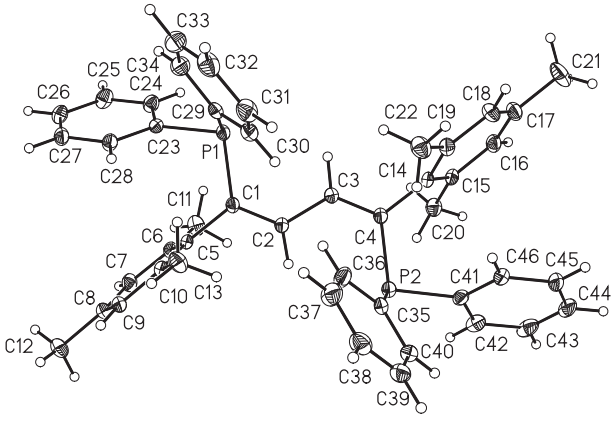


Fig. 6. Molecular structure and numbering scheme of 1,4-bis(2,4,6-trimethylphenyl)-1,4-bis(diphenylphosphanyl)-1,3-butadiene [(*Z,Z*)-**3$_{Mes}$**]. The ellipsoids represent a probability of 40%, H atoms are drawn with arbitrary radii. Selected bond lengths (pm): P1–C1 185.3(2), P1–C23 182.6(2), P1–C29 183.3(2), C1–C2 134.5(3), C2–C3 146.5(3), C3–C4 134.5(3), P2–C4 186.1(2), P2–C35 184.0(2), P2–C41 182.9(2), C1–C5 150.4(3), C4–C14 150.3(3); angles (°): C1–P1–C23 103.55(9), C1–P1–C29 103.54(9), C23–P1–C29 101.6(1), C4–P2–C35 103.66(9), C4–P2–C41 102.40(9), C35–P2–C41 101.6(1), P1–C1–C2 119.8(1), C1–C2–C3 126.7(2), C2–C3–C4 126.3(2), C3–C4–P2 119.3(1).

Table 5
Comparison of selected structural data of the NUPHOS diphosphanes $Ph_2P(R)C{=}CH{-}CH{=}C(R)PPh_2$ $\mathbf{3_{Me}}$ (R = Me), $\mathbf{3_{Ph}}$ (R = Ph) [34], and $\mathbf{3_{Silyl}}$ (R = $SiMe_3$) with crystallographic inversion symmetry.

	(*Z*,*Z*)-$\mathbf{3_{Me}}$	(*E*,*E*)-$\mathbf{3_{Ph}}$	(*E*,*E*)-$\mathbf{3_{Silyl}}$
C1–C1A	144.0(4)	143.9(9)	145.7(4)
C1–C2	135.0(3)	135.1(6)	135.3(3)
C2–Si1/C	150.0(3)	149.0(6)	189.8(2)
P1–C2	184.3(2)	183.0(5)	182.6(2)
P1–C3	184.0(2)	182.6(5)	183.0(2)
P1–C9	183.9(2)	183.3(5)	183.1(2)
C1A–C1–C2	126.6(3)	126.3(5)	125.4(2)
C1–C2–P1	119.5(2)	124.5(4)	121.0(1)
C1–C2–Si1/C	121.1(2)	123.1(4)	123.3(1)
P1–C2–Si1/C	119.4(2)	112.4(3)	115.4(1)
C2–P1–C3	101.88(9)	101.2(2)	103.86(8)
C2–P1–C9	101.22(9)	105.0(2)	101.98(9)
C3–P1–C9	101.94(9)	102.4(2)	103.97(9)

The isomer with neighbouring phosphanyl groups, 1,4-diphenyl-1,2-bis(diphenylphosphanyl)-1,3-butadiene (**4**), exhibits rather unusual NMR parameters (Scheme 4). The $^3J(H,H)$ coupling constant of 16.4 Hz is larger than those of **3** because both hydrogen atoms are members of the same alkene moiety whereas in **3** the coupling hydrogen pair belongs to different alkene units which are connected by a C–C single bond. This effect also leads to a large $^3J(P,P)$ coupling constant which exhibits an impressive value of 196.1 Hz. For the allene derivative 2,2,7,7-tetramethyl-3,6-bis(diphenylphosphanyl) octa-3,4-diene (**5**) the coupling constants are rather small. The hydrogen atom at the allene unit with a chemical shift of $\delta = 4.69$ shows a $^3J(H,H)$ value of 8.8 Hz and $^3J(H,P)$ and $^4J(H,P)$ coupling constants of 8.0 and 2.6 Hz, respectively. The hydrogen atom at the saturated chiral carbon atom with a chemical shift of $\delta = 2.86$ exhibits a small coupling with the phosphorus atom of $^2J(H,P) = 5.0$ Hz.

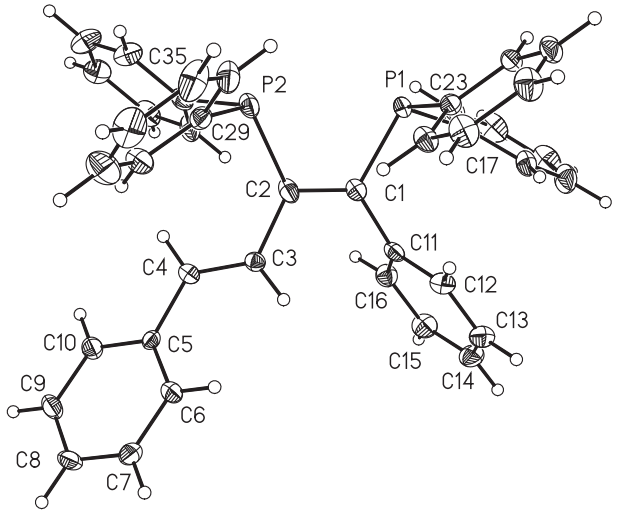


Fig. 7. Molecular structure and numbering scheme of 1,4-diphenyl-1,2-bis(diphenylphosphanyl)-1,3-butadiene (**4**). Disordering of the C3–C4 unit as well as of the attached phenyl group is omitted for clarity reasons. The ellipsoids represent a probability of 40%, H atoms are drawn with arbitrary radii. Selected bond lengths (pm): P1–C1 186.2(2), P1–C17 183.9(2), P1–C23 182.9(2), P2–C2 185.4(2), P2–C29 183.5(2), P2–C35 182.6(2), C1–C2 135.4(3), C1–C11 149.5(3), C2–C3 154.0(5), C3–C4 132.7(5), C4–C5 148.4(4); angles (°): C1–P1–C17 101.02(8), C1–P1–C23 101.24(9), C17–P1–C23 103.20(9), C2–P2–C29 104.34(9), C2–P2–C35 103.68(9), C29–P2–C35 104.44(9), P1–C1–C2 119.5(2), P1–C1–C11 117.6(1), C2–C1–C11 122.8(2), C1–C2–C3 116.9(2), C1–C2–P2 115.9(2), C3–C2–P2 125.9(2), C2–C3–C4 123.7(4), C3–C4–C5 127.1(4).

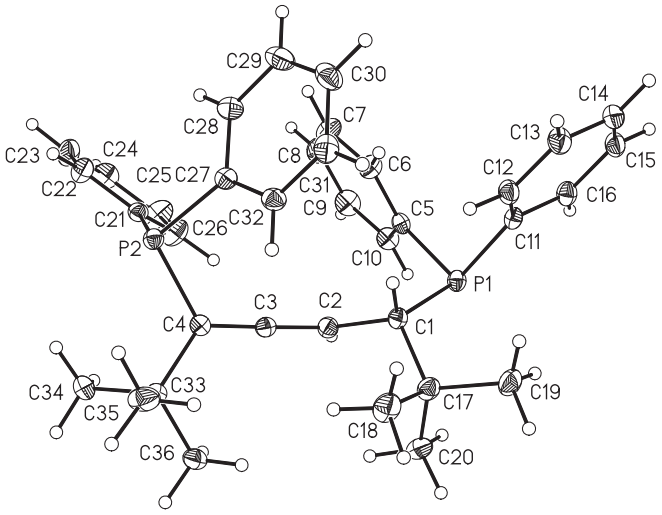


Fig. 8. Molecular structure and numbering scheme of 2,2,7,7-tetramethyl-3,6-bis(diphenylphosphanyl)octa-3,4-diene (**5**). The ellipsoids represent a probability of 40%, H atoms are drawn with arbitrary radii. Selected bond lengths (pm): P1–C1 188.0(2), P1–C5 183.2(2), P1–C11 184.2(2), P2–C4 185.0(2), P2–C21 183.3(2), P2–C27 183.0(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); angles (°): C1–P1–C5 101.9(1), C1–P1–C11 105.0(1), C5–P1–C11 99.7(1), C4–P2–C21 104.9(1), C4–P2–C27 102.50(9), C21–P2–C27 104.2(1), P1–C1–C2 108.0(2), P1–C1–C17 112.0(2), C2–C1–C17 113.4(2), C1–C2–C3 127.4(2), C2–C3–C4 177.3(2), C3–C4–P2 121.0(2), C3–C4–C33 123.4(2), P2–C4–C33 115.5(2).

2.4. Molecular structures

X-ray structures and numbering schemes of the bis(diphenylphosphanyl)-1,3-butadienes are displayed in Figs. 4–6. Selected structural parameters are summarized in Table 5 for those isomers which contain crystallographic inversion symmetry. The central 1,3-butadiene backbone contains two isolated C=C double bonds and a middle C–C single bond with bond lengths which are characteristic for sp^2-hybridized carbon atoms. Aryl groups R are oriented nearly perpendicular to the adjacent alkene unit and are not interacting with the butadiene π-system. Rather large C_{aryl}–C_{alkene} distances of 149.0 and 150.4 pm for (*E*,*E*)-$\mathbf{3_{Ph}}$ and (*Z*,*Z*)-$\mathbf{3_{Mes}}$, respectively, support this interpretation. The coordination spheres of the phosphorus atoms are trigonal pyramidal and the P–C distances are equal within the standard deviations excluding any P–C multiple bond character. In agreement with the Gillespie-Nyholm concept (that double bonds demand more space leading to a reduced distal and enlarged proximal angles in alkenes) the C1A–C1–C2 angles are significantly widened and the P1–C2–R angles are smaller than 120° (see Table 5).

Molecular structure and numbering scheme of 1,4-diphenyl-1,2-bis(diphenylphosphanyl)-1,3-butadiene (**4**) is displayed in Fig. 7. The structure is hampered by disordering of the C3–C4 moiety limiting the discussion of the structural parameters. The large vicinal diphenylphosphanyl groups do not induce a large steric strain because neither a lengthening of the C1–C2 double bond (135.3(3) pm) nor an enlargement of the C1–C2–P2 (115.9(2)°) and C2–C1–P1 angles (119.6(2)°) is observed. In contrast to the 1,4-phosphanylated derivatives the P1–C1 and P2–C2 bond lengths are larger than those to the phenyl substituents. The free electron pairs of the phosphanyl groups of **4** are oriented towards each other and are responsible for the exceptional large $^3J(P,P)$ coupling constant.

Molecular structure and numbering scheme of 2,2,7,7-tetramethyl-3,6-bis(diphenylphosphanyl)octa-3,4-diene (**5**) are represented in Fig. 8. The allene backbone shows very short C=C double bonds due to the enhanced *s*-orbital contribution of the middle *sp*-hybridyzed carbon atom C3. This allene fragment is nearly linear

(C2–C3–C4 177.3(2)°). Due to steric reasons the C–C bonds to the tert-butyl groups are slightly elongated compared to unstrained C–C single bonds.

3. Conclusion and summary

Catalytic calcium-mediated hydrophosphanylation reactions of butadiynes with diphenylphosphane yield a variety of compounds mainly depending on the bulkiness of the groups R at the butadiyne moieties. The investigation of this calcium-mediated hydrophosphanylation leads to the following conclusions:

(i) Quantum chemical investigations suggest that the first reaction step is the release of one THF molecule from the catalyst $[(thf)_4Ca(PPh_2)_2]$ in order to create an available coordination site. After addition of a Ca–P bond to the C≡C triple bond a hexa-coordinate calcium complex is regained due to coordination to three THF ligands, two phosphorus atoms and one carbon atom.
(ii) Only the two-fold addition of $HPPh_2$ to the butadiyne was observed. Neither products of a single addition (maintaining one of the triple bonds) were detected nor products with three or more PPh_2 substituents. This observation suggests that the addition of the first $HPPh_2$ leads to an activation of the remaining C≡C triple bond whereas the C=C double bonds proved to be inert towards calcium-mediated hydrophosphanylation.
(iii) Constitution: products of the twofold addition of $HPPh_2$ to the butadiynes include 1,4-bis(diphenylphosphanyl)-1,3-butadienes, 1,2-bis(diphenylphosphanyl)-1,3-butadienes, and 1,4-bis(diphenylphosphanyl)buta-1,2-dienes, whereas 2,3-bis(diphenylphosphanyl)-1,3-butadienes were not observed at all. The addition of the PPh_2 group in 1-position and of the $(thf)_3CaPPh_2$ fragment in 2-position is favoured due to steric and electronic reasons. A similar steric reason could be responsible for the observation that hydrophosphanylation at C3 is disadvantageous.
(iv) Configuration: based on the fact that an ionic mechanism seems to be likely (due to the lack of formation of tetraphenyldiphosphane) the first reaction step is a *cis*-addition of a Ca–P bond to the C≡C triple bond. However, the *E*-isomer is not favoured compared to the *Z*-isomer. This fact suggests a fast relaxation process compared to the second diphenylphosphane addition step *via* a 1,3-shift of the $(thf)_3CaPPh_2$ unit or a dissociation into solvent separated ions. Quantum chemical investigations indeed support this dynamic process because the energy differences of these isomers are very small.

The calcium-mediated hydrophosphanylation is an easy and fast method to heterofunctionalize butadiynes. Even though, diverse products are obtained, crystallization allows the isolation of one of the products. Crystal structure determinations of these butadienes show that the phosphorus atoms are in pyramidal environments. This fact allows the use of these diphosphanylbutadienes as ligands (1,4-substituted NUPHOS ligands) in transition metal coordination chemistry and catalysis. Future investigations will deal with solvent effects because stronger Lewis bases than THF will bind stronger to the cation which should slow down the reaction and hence, might enhance the selectivity.

4. Experimental

4.1. General remarks

All manipulations were carried out under 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 ^1H, $^{13}C\{^1H\}$, and ^{31}P NMR spectra were obtained on a Bruker AC 400 MHz or a Bruker 200 MHz spectrometer. Mass spectra were obtained on a Finnigan MAT SSQ 710 system, and IR measurements were carried out using a Perkin-Elmer System 2000 FTIR. The IR spectra were taken as Nujol mulls between KBr windows. Melting and decomposition points were measured with a Reichert-Jung apparatus type 302102 and are uncorrected. The catalyst $[(thf)_4Ca(PPh_2)_2]$ **1** was prepared according to a literature procedure [13,14].

4.2. Synthesis of 1,2-diphenyl-1-diphenylphosphanylethene (*2a*)

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 **1** were added. The colorless reaction mixture turned orange immediately. This solution was warmed to room temperature and stirred for 1 h. Then all volatiles were removed and the residue washed twice with 25 ml of ether in order to obtain 1.42 g of colorless **2a** (3.9 mmol, 77%). Physical data were in agreement with literature values [35].

4.3. Synthesis of diphenyl-(1-phenylprop-1-enyl)phosphane (*2b*)

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 **1** were added. The colorless solution turned yellow. The reaction mixture was stirred at room temperature and then heated under reflux for additional 5 h. 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 colorless crystals of **2b** (1.69 mmol, 85%) precipitated. Physical data were in agreement with literature values [36,37].

4.4. Synthesis of 2,5-bis(diphenylphosphanyl)hexa-2,4-diene (3_{Me})

2,4-Hexadiyne (0.22 g, 2.82 mmol) in 18 ml of THF was cooled to −78 °C. $HPPh_2$ (0.98 ml, 1.0 g, 5.63 mmol) and 5 mol-% of $[(thf)_4Ca(PPh_2)_2]$ (**1**) were added. The colorless solution turned yellow and was stirred at room temperature for 2 h and then under reflux for 4 hours. Reduction of the volume to half of the original volume, addition of methanol and storage at −15 °C for one day led to the formation of colorless crystals of compound $\mathbf{3_{Me}}$ (1.03 g, yield 81%, mixture of isomers).

4.5. Physical data of *(Z,Z)-3_{Me}*

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, $CDCl_3$): $\delta = 7.66$ (CH, AA′XX′ type, see Table 4), 7.2–7.5 (m, Ph), 1.68 (m, Me). $^{13}C\{^1H\}$ NMR (150.908 MHz, $CDCl_3$, X-part of AA′X patterns): $\delta = 23.4$ (Me), 128.3 (p-C, Ph), 128.4 (m-C, Ph), 133.1 (o-C, Ph), 135.4 (C=C–Me), 136.3 (i-C, Ph), 139.5 (C=C-H). ^{31}P NMR (81.013 MHz, $CDCl_3$): $\delta = -10.6$. 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 79.70, H 6.03.

4.6. Synthesis of 1,4-bis(diphenylphosphanyl)-1,4-bis(trimethylsilyl)-1,3-butadiene (3_{Silyl})

$HPPh_2$ (0.89 ml, 2.06 mmol) and 5 mol-% of **1** 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 colorless solution turned red

immediately. After stirring at room temperature for 1 h and under reflux for additional 6 h, the volume was reduced to half of the original volume. A few milliliters of methanol were added and the reaction mixture stored at −15 °C. Colorless crystals of **3$_{Silyl}$** (0.46 g, 0.81 mmol, 79%, mixtures of isomers) precipitated and were collected.

4.7. Physical data of (*E,E*)-**3$_{Silyl}$**

M.p. 93–96 °C. MS (EI): 466 $[M]^+$ (1%), 389 $[M-PPh_2]^+$ (100%), 183 $[PPh_2-2\ H]^+$ (20%). ^{1}H NMR (200.13 MHz, $CDCl_3$): $\delta = -0.25$ ($SiMe_3$), 6.56 (CH, AA′XX′ type, see Table 4), 7.2–7.5 (phenyl). ^{13}C{^{1}H} NMR (150.908 MHz, $CDCl_3$): $\delta = 0.3$ ($SiMe_3$), 128.6 (m-C, Ph), 129.0 (p-C, Ph), 134.6 (o-C, Ph), 135.9 (i-C, Ph), 145.1 (C═C), 147.0 (C═C). ^{31}P NMR (81.01 MHz, $CDCl_3$): $\delta = +6.3$. 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.

4.8. Synthesis of 1,4-bis(diphenylphosphanyl)-1,4-dimesityl-1,3-butadiene (**3$_{Mes}$**)

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 $[(thf)_4Ca(PPh_2)_2]$ (**1**) were added, and the solution was stirred at room temperature for 2 h. Then the volume was reduced to half of the original volume and 6 ml of methanol were added. After 2 days colorless crystals of **3$_{Mes}$** were obtained at room temperature (0.28 g, 76%, mixture of isomers).

4.9. Physical data of (*Z,Z*)-**3$_{Mes}$**

M.p. 220–223 °C. MS (EI): 658 $[M]^+$ (40%), 473 $[M-PPh_2]^+$ (60%), 183 $[PPh_2-2\ H]^+$ (80%). ^{1}H NMR (400.25 MHz, $CDCl_3$): $\delta = 1.87$ (o-Me, Mes), 2.17 (p-Me, Mes), 5.98 (CH, AA′XX′ type, see Table 4), 6.60 (C_6H_2, Mes), 7.1–7.4 (Ph). ^{31}P NMR (81.013 MHz, $CDCl_3$): $\delta = -1.7$. 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.

4.10. Synthesis of 1,4-diphenyl-1,4-bis(diphenylphosphanyl)-1,3-butadiene (**3$_{Ph}$**) and 1,4-diphenyl-1,2-bis(diphenylphosphanyl)-1,3-butadiene (**4**)

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 **1** were added and the solution was stirred at room temperature for 2 h. Then the volume was reduced to half of the original volume and cooled to −15 °C. After one day 0.72 g of crystals (1.25 mmol, 89%, mixture of isomers) precipitated and were collected. Fractionated crystallization gave (*E,E*)-**3$_{Ph}$** and thereafter another crop of crystalline **4**.

4.11. Physical data of (*E,E*)-**3$_{Ph}$**

M.p. 216–220 °C. MS (EI): 574 $[M]^+$ (1%), 389 $[M-PPh_2]^+$ (100%), 183 $[PPh_2-2\ H]^+$ (20%). ^{1}H NMR (400.25 MHz, $CDCl_3$): $\delta = 6.12$ (CH), 7.0–7.4 (Ph). ^{13}C{^{1}H} NMR (150.908 MHz, $CDCl_3$): $\delta = 126.7$ (p-C, Ph), 127.9 (p-C, PPh), 128.0 (m-C, Ph), 128.3 (m-C, PPh), 129.7 (o-C, Ph), 133.9 (i-C, Ph), 134.2 (o-C, PPh), 135.2 (i-C, PPh), 139.3 (C═C), 143.6 (C═C). ^{31}P NMR (81.013 MHz, $CDCl_3$): $\delta = +7.8$. 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.

4.12. Physical data of **4**

M.p. 157 °C. MS (EI): 574 $[M]^+$ (70%), 497 $[M-Ph]^+$ (10%), 370 $[P_2Ph_4]^+$ (100%), 287 (23%), 183 (52%), 108 (4%). ^{1}H NMR (400.25 MHz, $CDCl_3$): $\delta = 6.06$ ($^3J_{H,H} = 16.4$ Hz), 6.49 ($^3J_{H,H} = 16.4$, $^3J_{H,P} = 3.8$), 6.6–7.6 (Ph). ^{31}P{^{1}H} NMR (81.013 MHz, $CDCl_3$): $\delta = +4.2$, −5.5, $^3J_{P,P} = 196.1$ Hz. IR (Nujol): 1593 w, 1581 w, 1572 w, 1305 m, 1152 w, 1068 w, 1022 m, 966 m, 803 w, 751 s, 738 vs, 692 vs. Elemental analysis ($C_{40}H_{32}P_2$, 574,630): calc.: C 83.61, H 5.61; found: C 83.21, H 5.47.

Table 6
Crystal data and refinement details for the X-ray crystal structure determinations of (*Z*)-1-phenyl-2-diphenylphosphanyl-1-propene (**2b**) and doubly hydrophosphanylated butadiynes.

Compound	**2b**	(*Z,Z*)-**3$_{Me}$**	(*E,E*)-**3$_{Silyl}$**	(*Z,Z*)-**3$_{Mes}$**	(*Z,E*)-**4**	**5**
Formula	$C_{21}H_{19}P$	$C_{30}H_{28}P_2$	$C_{34}H_{40}P_2Si_2$	$C_{46}H_{44}P_2$	$C_{40}H_{32}P_2$	$C_{36}H_{40}P_2$
F_w, g mol^{-1}	302.33	450.46	566.78	658.75	574.60	534.62
T, K	−90(2)	−90(2)	−90(2)	−90(2)	−90(2)	−90(2)
Crystal system	Monoclinic	Tetragonal	Monoclinic	Triclinic	Triclinic	Triclinic
Space group	P 2$_1$/c	I 4$_1$/a	P 2$_1$/c	P ī	P ī	P ī
a, Å	5.9484(3)	24.0265(12)	12.2046(7)	9.8621(5)	11.0401(5)	10.0187(8)
b, Å	17.9623(8)	24.0265(12)	11.1734(5)	12.5438(4)	11.4504(5)	10.2630(8)
c, Å	15.4154(8)	8.4030(5)	11.8562(5)	16.5100(5)	13.9940(7)	15.6487(9)
α, deg	90	90	90	109.259(2)	104.332(2)	91.435(4)
β, deg	94.111(3)	90	96.376(3)	93.233(2)	95.433(2)	106.188(4)
γ, deg	90	90	90	103.269(2)	114.212(2)	99.927(4)
V, Å^3	1642.85(14)	4850.8(4)	1606.79(14)	1857.15(13)	1524.18(13)	1517.55(19)
Z	4	8	2	2	2	2
ρ, g cm^{-3}	1.222	1.234	1.171	1.178	1.252	1.170
μ, mm^{-1}	1.62	1.95	2.31	1.48	1.71	1.66
Measured data	10775	15324	9716	13655	10366	10446
Data with $I \geq 2\sigma(I)$	2743	1828	2966	5214	4442	4006
Unique data (R_{int})	3744/0.0432	2772/0.1020	3615/0.0426	8451/0.0378	6792/0.0330	6793/0.0468
wR_2 (all data, on F^2)[a]	0.1088	0.1114	0.1179	0.1367	0.1328	0.1202
R_1 ($I \geq 2\sigma(I)$)[a]	0.0406	0.0476	0.0450	0.0521	0.0472	0.0533
S[b]	1.003	1.005	1.014	1.004	0.873	0.984
Res. dens./e Å^{-3}	0.210/−0.350	0.253/−0.216	1.248/−0.264	0.320/−0.298	0.258/−0.318	0.237/−0.244
CCDC No.	779117	779118	779119	779120	779121	779122

[a] Definition of the R indices: $R_1 = (\sum ||F_o| - |F_c||)/\sum |F_o|$; $wR_2 = \{\sum[w(F_o^2 - F_c^2)^2]/\sum[w(F_o^2)^2]\}^{1/2}$ with $w^{-1} = \sigma^2(F_o^2) + (aP)^2 + bP$; $P = [2F_c^2 + \text{Max}\ F_o^2]/3$.
[b] $S = \{\sum[w(F_o^2 - F_c^2)^2]/(N_o - N_p)\}^{1/2}$.

4.13. Synthesis of 3,6-bis(diphenylphosphanyl)-2,2,7,7-tetrametylocta-3,5-diene (**3$_{tBu}$**) and 3,6-bis(diphenylphosphanyl)-2,2,7,7-tetrametylocta-3,4-diene (**5**)

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 $[(thf)_4Ca(PPh_2)_2]$ (**1**) 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 a mixture of (*Z,Z*)-**3$_{tBu}$** and **5** was obtained at room temperature (0.91 g, 69%). The physical data of **5** were determined from crystalline material, whereas (*Z,Z*)-**3$_{tBu}$** was always contaminated with **5**.

4.14. Physical data of (Z,Z)-**3$_{tBu}$**

^{1}H NMR (200.13 MHz, $CDCl_3$): $\delta = 0.93$ (*t*Bu), 7.01 (C═CH), 7.1–7.5 (Ph). $\delta = {}^{31}$P NMR (81.013 MHz, $CDCl_3$): $\delta = -5.6$.

4.15. Physical data of **5**

M.p. 148–151 °C. MS (EI): 534 $[M]^+$ (1%), 477 $[M-{}^tBu]^+$, 349 $[M-PPh_2]^+$ (100%), 293 $[349-{}^tBu]^+$ (20%), 183 $[PPh_2-2H]^+$ (60%). ^{1}H NMR (200.13 MHz, $CDCl_3$): $\delta = 1.02$ (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{^{1}H} NMR (50.328 MHz, $CDCl_3$): $\delta = 29.0$ ($J = 9.7$), 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, $CDCl_3$): $\delta = -2.3$, -7.1. IR (KBr): 2090 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.

4.16. X-ray structure determinations

The intensity data for the compounds were collected on a Nonius Kappa CCD diffractometer using graphite-monochromated Mo-K_α radiation. Data were corrected for Lorentz and polarization effects but not for absorption effects [47,48]. The structures were solved by direct methods (SHELXS [49]) and refined by full-matrix least squares techniques against F_o^2 (SHELXL-97 [49]). All hydrogen atoms of the compounds **2b**, **3$_{Me}$** as well as the ethyne hydrogen atoms of **3$_{Silyl}$**, **3$_{Mes}$** and **5** were located by difference Fourier synthesis and refined isotropically. All other hydrogen atoms were included at calculated positions with fixed thermal parameters. The ethene group C3–C4 and the attached phenyl-group of **4** were disordered. Two alternative sites were refined with occupancies of 62(2) and 38(2)%. The disordered phenyl-groups of **4** were refined as rigid-groups. All non-disordered, non-hydrogen atoms were refined anisotropically [49].

Crystallographic data as well as structure solution and refinement details are summarized in Table 6. XP (SIEMENS Analytical X-ray Instruments, Inc.) was used for structure representations.

4.17. Quantum chemical calculations

Quantum chemical calculations were carried out with the Turbomole 5.10 program [50]. Structural optimizations were driven by the structure optimization procedure of the Gaussian 03 program package [51]. The molecular geometries were first optimized with BP86/TZVP [52,53], subsequently with B97-D/TZVPP [54–56], both in combination with the resolution of identity (`RI`) density fitting technique [57]. Molecular structures were visualized with the Pymol program [58]. Reaction energies have not been corrected for basis set superposition effects.

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Appendix A. Supporting information

Crystallographic data (excluding structure factors) has been deposited with the Cambridge Crystallographic Data Centre as supplementary publication CCDC-779117 for **2b**, CCDC-779118 for **3$_{Me}$**, CCDC-779119 for **3$_{Silyl}$**, CCDC-779120 for **3$_{Mes}$**, CCDC-779121 for **4**, and CCDC-779122 for **5**. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK [E-mail: deposit@ccdc.cam.ac.uk].

References

[1] S. Doherty, J.G. Knight, E.G. Robins, T.H. Scanlan, P.A. Champkin, W. Clegg, J. Am. Chem. Soc. 123 (2001) 5110–5111.
[2] S. Doherty, E.G. Robins, M. Nieuwenhuyzen, J.G. Knight, P.A. Champkin, W. Clegg, Organometallics 21 (2002) 1383–1399.
[3] S. Doherty, J.G. Knight, C.H. Smyth, R.W. Harrington, W. Clegg, Organometallics 26 (2007) 6453–6461.
[4] S. Doherty, P. Goodrich, C. Hardacre, H.-K. Luo, D.W. Rooney, K.R. Seddon, P. Styring, Green Chem. 6 (2004) 63–67.
[5] S. Doherty, C.R. Newman, R.K. Rath, J.-A. van den Berg, C. Hardacre, M. Nieuwenhuyzen, J.G. Knight, Organometallics 23 (2004) 1055–1064.
[6] S. Doherty, J.G. Knight, R.K. Rath, W. Clegg, R.W. Harrington, C.R. Newman, R. Campbell, H. Amin, Organometallics 24 (2005) 2633–2644.
[7] K. Izod, W. McFarlane, B.V. Tyson, W. Clegg, R.W. Harrington, Chem. Commun. (2004) 570–571.
[8] K. Wimmer, C. Birg, R. Kretschmer, T.M.A. Al-Shboul, H. Görls, S. Krieck, M. Westerhausen, Z. Naturforsch. 64b (2009) 1360–1368.
[9] Selected reviews: (a) D. Julienne, O. Delacroix, A.-C. Gaumont, Curr. Org. Chem. 14 (2010) 457–482;
(b) H. Yorimitsu, K. Oshima, Pure & Appl. Chem. 78 (2006) 441–449;
(c) O. Delacroix, A.C. Gaumont, Curr. Org. Chem. 9 (2005) 1851–1882;
(d) C.-J. Li, Chem. Rev. 105 (2005) 3095–3165;
(e) J.-L. Montchamp, J. Organomet. Chem. 690 (2005) 2388–2406;
(f) G. Togni, H. Grützmacher, Catalytic Heterofunctionalization. Wiley-VCH, Weinheim, 2001.
[10] (a) A.-C. Gaumont, A. Simon, J.-M. Denis, Tetrahedron Lett. 39 (1998) 985–988;
(b) D. Mimeau, A.-C. Gaumont, J. Org. Chem. 68 (2003) 7016–7022.
[11] (a) K. Takaki, G. Koshoji, K. Komeyama, M. Takeda, T. Shishido, A. Kitani, K. Takehira, J. Org. Chem. 68 (2003) 6554–6565;
(b) K. Takaki, K. Komeyama, D. Kobayashi, T. Kawabata, K. Takehira, J. Alloys Compd. 408–412 (2006) 432–436.
[12] K. Komeyama, D. Kobayashi, Y. Yamamoto, K. Takehira, K. Takaki, Tetrahedron 62 (2006) 2511–2519.
[13] M. Gärtner, H. Görls, M. Westerhausen, Z. Anorg. Allg. Chem. 633 (2007) 2025–2031.
[14] M.R. Crimmin, A.G.M. Barrett, M.S. Hill, P.B. Hitchcock, P.A. Procopiou, Inorg. Chem. 46 (2007) 10410–10415.
[15] M. Gärtner, H. Görls, M. Westerhausen, Inorg. Chem. 47 (2008) 1397–1405.
[16] T.P. Hanusa, Coord. Chem. Rev. 210 (2000) 329–367.
[17] J.S. Alexander, K. Ruhlandt-Senge, Eur. J. Inorg. Chem. (2002) 2761–2774.
[18] (a) M. Westerhausen, Coord. Chem. Rev. 176 (1998) 157–210;
(b) M. Westerhausen, Angew. Chem. Int. Ed. 40 (2001) 2975–2977;
(c) M. Westerhausen, Dalton Trans. (2006) 4755–4768;
(d) M. Westerhausen, M. Gärtner, R. Fischer, J. Langer, L. Yu, M. Reiher, Chem. Eur. J. 13 (2007) 6292–6306;
(e) M. Westerhausen, M. Gärtner, R. Fischer, J. Langer, Angew. Chem. Int. Ed. 46 (2007) 1950–1956;
(f) M. Westerhausen, Coord. Chem. Rev. 252 (2008) 1516–1531.
[19] C. Eaborn, S.A. Hawkes, P.B. Hitchcock, J.D. Smith, Chem. Commun. (1997) 1961–1962.
[20] P.B. Hitchcock, A.V. Khvostov, M.F. Lappert, J. Organomet. Chem. 663 (2002) 263–268.

[21] (a) M. Kaupp, Angew. Chem. Int Ed. 40 (2001) 3534–3565;
(b) R.J. Gillespie, S. Noury, J. Pilmé, B. Silvi, Inorg. Chem. 43 (2004) 3248–3256.
[22] (a) A.G.M. Barrett, M.R. Crimmin, M.S. Hill, P.A. Procopiou, Proc. R. Soc. A 466 (2010) 927–963;
(b) S. Harder, Chem. Rev. 110 (2010) 3852–3876.
[23] M.R. Crimmin, I.J. Casely, M.S. Hill, J. Am. Chem. Soc. 127 (2005) 2042–2043.
[24] S. Datta, P.W. Roesky, S. Blechert, Organometallics 26 (2007) 4392–4394.
[25] S. Datta, M.T. Gamer, P.W. Roesky, Organometallics 27 (2008) 1207–1213.
[26] F. Buch, S. Harder, Z. Naturforsch. 63b (2008) 169–177.
[27] F. Buch, J. Brettar, S. Harder, Angew. Chem. Int. Ed. 45 (2006) 2741–2745.
[28] M.R. Crimmin, A.G.M. Barrett, M.S. Hill, P.B. Hitchcock, P.A. Procopiou, Organometallics 26 (2007) 2953–2956.
[29] M.R. Crimmin, A.G.M. Barrett, M.S. Hill, P.B. Hitchcock, P.A. Procopiou, Organometallics 27 (2008) 497–499.
[30] M.R. Crimmin, A.G.M. Barrett, M.S. Hill, P.A. Procopiou, Org. Lett. 9 (2007) 331–333.
[31] A. Zuyls, P.W. Roesky, G.B. Deacon, K. Konstas, P.C. Junk, Eur. J. Inorg. Chem. (2008) 693–697.
[32] J. Spielmann, F. Buch, S. Harder, Angew. Chem. Int. Ed. 47 (2008) 9434–9438.
[33] U. Kazmaier, Angew. Chem. Int. Ed. 48 (2009) 5790–5792 and lit. cited therein.
[34] T.M.A. Al-Shboul, H. Görls, M. Westerhausen, Inorg. Chem. Commun. 11 (2008) 1419–1421.
[35] M. Taillefer, H.J. Cristau, A. Fruchier, V. Vicente, J. Organomet. Chem. 624 (2001) 307–315.
[36] J.L. Bookham, W. McFarlane, M. Thornton-Pett, S. Jones, J. Chem. Soc., Dalton Trans. (1990) 3621–3627.
[37] J.L. Bookham, D.M. Smithies, A. Wright, M. Thornton-Pett, W. McFarlane, J. Chem. Soc., Dalton Trans. (1998) 811–818.
[38] M. Westerhausen, M.H. Digeser, H. Nöth, T. Seifert, A. Pfitzner, J. Am. Chem. Soc. 120 (1998) 6722–6725.
[39] K. Komeyama, T. Kawabata, K. Takehira, K. Takaki, J. Org. Chem. 70 (2005) 7260–7266.
[40] K. Takaki, M. Takeda, G. Koshoji, T. Shishido, K. Kakehira, Tetrahedron Lett. 42 (2001) 6357–6360.
[41] K. Takaki, G. Koshoji, K. Komeyama, M. Takeda, T. Shishido, A. Kitani, K. Takehira, J. Org. Chem. 68 (2003) 6554–6565.
[42] K. Komeyama, D. Kobayashi, Y. Yamamoto, K. Takehira, K. Takaki, Tetrahedron 62 (2006) 2511–2519.
[43] R.A. Williams, T.P. Hanusa, J.C. Huffman, J. Am. Chem. Soc. 112 (1990) 2454–2455.
[44] M. Westerhausen, M.H. Digeser, H. Nöth, W. Ponikwar, T. Seifert, K. Polborn, Inorg. Chem. 38 (1999) 3207–3214.
[45] A.M. Aguiar, T.G. Archibald, Tetrahedron Lett. 7 (1966) 5541–5546.
[46] M.A. Kazankova, I.V. Efimova, A.N. Kochetkov, V.V. Afanas'ev, I.P. Beletskaya, P.H. Dixneuf, Synlett (2001) 497–500.
[47] COLLECT, Data Collection Software. Nonius B.V., Netherlands, 1998.
[48] Z. Otwinowski, W. Minor, Processing of X-ray diffraction data collected in oscillation mode. in: C.W. Carter, R.M. Sweet (Eds.), Methods in Enzymology, Macromolecular Crystallography, Part A, vol. 276. Academic Press, 1997, pp. 307–326.
[49] G.M. Sheldrick, Acta Cryst. A64 (2008) 112–122.
[50] R. Ahlrichs, M. Bär, M. Häser, H. Horn, C. Kölmel, Chem. Phys. Lett. 162 (1989) 165–169.
[51] M.J. Frisch, et al., Gaussian 03, (Revision D.01). Gaussian, Inc., Wallingford CT, 2004.
[52] A.D. Becke, Phys. Rev. A 38 (1988) 3098–3100.
[53] J.P. Perdew, Phys. Rev. B 33 (1986) 8822–8824.
[54] S. Grimme, J. Comp. Chem. 25 (2004) 1463–1473.
[55] A. Schäfer, C. Huber, R. Ahlrichs, J. Chem. Phys. 100 (1994) 5829.
[56] F. Weigend, M. Häser, H. Patzelt, R. Ahlrichs, Chem. Phys. Lett. 294 (1998) 143–152.
[57] K. Eichkorn, O. Treutler, H. Öhm, M. Häser, R. Ahlrichs, Chem. Phys. Lett. 242 (1995) 652–660.
[58] The PyMOL Molecular Graphics System, Version 1.2r3pre. Schroedinger, LLC, 2002.http://pymol.sourceforge.net.