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

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Z. Naturforsch. **2009**, *64b,* 1360 – 1368; received September 17, 2009

Dedicated to Professor Hubert Schmidbaur on the occasion of his 75th birthday

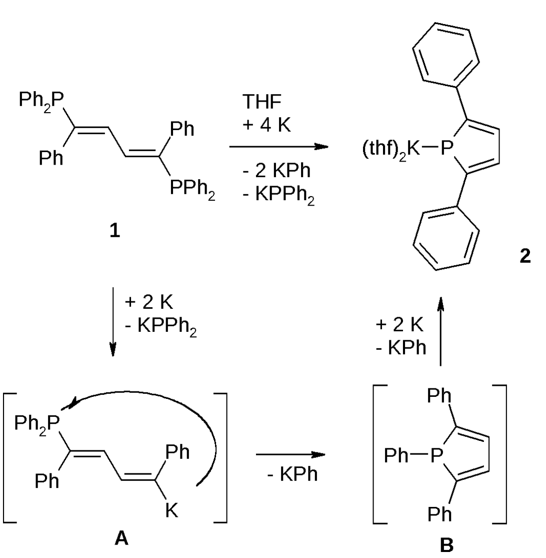
The reduction of 1,4-diphenyl-1,4-bis(diphenylphosphanyl)buta-1,3-diene (**1**) (1,4-diphenyl-NUPHOS) with potassium in THF yields bis(THF)potassium 2,5-diphenylphospholide (**2**) which crystallizes with a chain structure. The metathesis reaction of **2** with the iodides of calcium, strontium, and barium leads to the formation of [bis(THF)calcium bis(2,5-diphenylphospholide)] (**3**), [bis(THF)strontium bis(2,5-diphenylphospholide)] (**4**), and [bis(THF)barium bis(2,5-diphenylphospholide)] (**5**). The reaction of $M\{P(H)Si\textit{i}Pr_3\}_2$ with diphenylbutadiyne in THF also leads to the formation of the 2,5-diphenylphospholides of calcium (**3**), strontium (**4**), and barium (**5**). The molecular structures of **2** to **4** are discussed. The environment of the metal atoms is very similar in all these compounds: The metal atoms show an η^5 coordination to the phospholide rings forming a bent sandwich complex. The open coordination site is occupied by two THF molecules.

Key words: Calcium, Potassium, Strontium, Phospholide, Sandwich Complexes, Salt Metathesis Reactions

Introduction

There is a vastly growing interest in organo calcium compounds due to many reasons [1]. The organic chemistry of the heavy alkaline earth metals shows an intermediate behavior between typical *s*-block elements and early transition metals because the compounds are mainly of ionic nature (*s*-block behavior) with the possibility to employ *d* orbitals for bonding (feature of transition metals) [2]. In the last few years also the catalytic activity gained on importance such as *e. g.* alkene [3] and lactide polymerization [4] as well as hydroamination [5] and hydrophosphanylation reactions [6 – 8] of multiple bonds. Thus, the addition of diphenylphosphane to diphenylbutadiyne was catalyzed effectively by easily accessible $[(thf)_4Ca(PPh_2)_2]$ [9] yielding 1,4-diphenyl-1,4-bis(diphenylphosphanyl)buta-1,3-diene (1,4-diphenyl-NUPHOS) (**1**) [8]. Finally, calcium is a non-toxic metal regardless of its concentration.

The compound classes of vinylphosphanes and especially of 1,4-bis(diphenylphosphanyl)buta-1,3-dienes (NUPHOS) play an important role as ligands at catalytically active metal atoms. NUPHOS ligands were prepared firstly by Doherty and coworkers [10] *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) [11] and 2,2′-bis(diphenylphosphanyl)biphenyl (BIPHEP) [12] clarify 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. Diphenylvinylphosphanes can also be reductively coupled by alkali metals such as *e. g.* lithium, yielding 1,4-bis(diphenylphosphanyl)butanes [13]. This reaction in mind we were looking at the redox behavior of 1,4-diphenyl-NUPHOS (**1**) and noticed during our electrochemical investigations that oxidation and reduction of this compound were irreversible processes. Therefore, we investigated the reaction of **1** with potassium in order to understand the reduction of **1**. However, 1,4-diphenyl-NUPHOS (**1**) contains several functionalities which



Scheme 1.

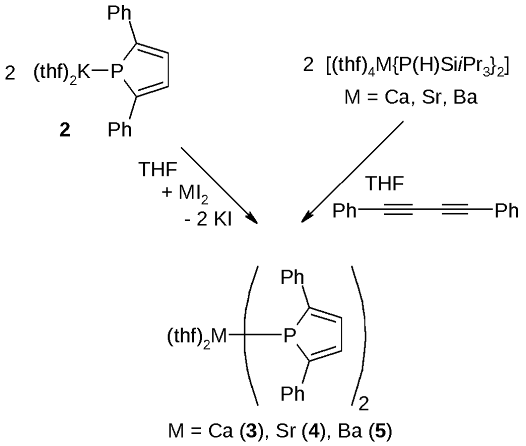
can be reduced. On the one hand, reduction of the butadiene backbone could lead to a but-2-ene-1,4-diide, but this redox reaction should be reversible. On the other hand, reaction of **1** with potassium could also lead to P–C bond cleavage reactions (which are well-known from the investigations of Issleib and Völker [14]).

Results and Discussion

Synthesis

Excess of potassium metal was stirred with 1,4-diphenyl-NUPHOS (**1**) in THF at r. t. Brown cords developed at the metal surface, and the reaction mixture turned dark red-brown. After three hours excess of potassium metal was removed, and the volume of the filtrate was reduced to a few milliliters. Upon cooling of this mother liquor colorless crystals of polymeric [bis(tetrahydrofuran)potassium 2,5-diphenylphospholide] (**2**) precipitated (Scheme 1). In 1,4-dioxane the reaction mixture had to be refluxed in order to give the desired phospholides whereas in refluxing toluene no reaction was observed. The reason for the strong dependency on the solvent could be the donor strength of the solvent. Ethers are able to stabilize this potassium phospholide whereas in arenes the formation of phospholides was not supported.

The initial reaction step could be the cleavage of a P–C bond yielding $KPPh_2$ and intermediate **A**. The carbanion now attacks the remaining phosphorus atom leading to the formation of KPh and 1,2,5-triphenylphosphole (**B**). The last reaction



Scheme 2.

sequence is well investigated starting from 1,2,5-triphenylphosphole (**B**) [15]; the reaction of **B** with potassium yields **2** and phenyl potassium. Alkali metals do not lead to a ring opening but exclusively to the elimination of the P-bound phenyl group and the formation of phospholides [16]. In order to detect also intermediate **A** an aliquot of the reaction solution was hydrolized and investigated with GC-MS methods. Besides benzene (hydrolysis of KPh) and $HPPh_2$ (from $KPPh_2$) also small amounts of PPh_3 and $Ph_2PC(Ph){=}CH{-}CH{=}C(H)Ph$ were detected supporting the proposed reaction mechanism. Addition of 1,4-dioxane (diox) to another aliquot of the reaction mixture gave polymeric $[(diox)_2KPPh_2]_\infty$ with an identical crystal structure as reported earlier [17].

The salt-metathesis reaction of potassium phospholide **2** with anhydrous alkaline earth metal diiodides in THF yields corresponding [bis(tetrahydrofuran-*O*)calcium bis(2,5-diphenylphospholide)] (**3**) and the homologous strontium (**4**) and barium derivatives (**5**) within a few minutes due to the insolubility of KI in this solvent. Alkaline earth metal bis{2,5-diphenyl-3,4-bis(trimethylsilyl)phospholides} are also accessible by the addition of diphenylbutadiyne to $[(thf)_4M\{P(SiMe_3)_2\}_2]$ in THF with the trimethylsilyl groups migrating from the P atom to the carbon atoms [18]. In these complexes the phospholide anions show a η^1 coordination to the alkaline earth metals with M–P σ bonds. Larger trialkylsilyl substituents avoid the 1,3-silyl shift and prefer intermolecular exchange reactions. Thus, the reaction of $[(thf)_4Ca\{As(H)Si\textit{i}Pr_3\}_2]$ with diphenylbutadiyne yields [bis(tetrahydrofuran-*O*)calcium bis(2,5-diphenylarsolide)] besides $Ca\{As(Si\textit{i}Pr_3)_2\}_2$ and other by-

Table 1. Comparison of the NMR data of [(thf)$_2$K(PC$_4$H$_2$-2,5-Ph$_2$)]$_\infty$ (**2**), [(thf)$_2$Ca(PC$_4$H$_2$-2,5-Ph$_2$)$_2$] (**3**), [(thf)$_2$Sr-(PC$_4$H$_2$-2,5-Ph$_2$)$_2$] (**4**), [(thf)$_2$Ba(PC$_4$H$_2$-2,5-Ph$_2$)$_2$] (**5**) and [(thf)$_2$Yb(PC$_4$H$_2$-2,5-Ph$_2$)$_2$] (**C**) [23] (chemical shifts in ppm, coupling constants in Hz).

	2	**3**	**4**	**5**	**C**
M	K	Ca	Sr	Ba	Yb
^{1}H:					
δ(C3,4-H)	6.71	7.30	7.27	7.05	7.26
δ(*o*-Ph)	7.68	7.67	7.64	7.62	7.67
δ(*m*-Ph)	7.41	7.23	7.23	7.19	7.23
δ(*p*-Ph)	6.36	7.06	7.11	6.99	7.07
^{13}C{^{1}H}:					
δ(C3,4)	127.3	125.1	124.9	124.3	120.3
^2J(P,C)	5.6	< 1	< 1	< 1	< 1
δ(C2,5)	159.2	151.6	152.8	153.0	151.9
^1J(P,C)	53.7	44.8	45.3	40.7	46
δ(*i*-Ph)	129.2	140.6	140.5	141.3	141.1
^2J(P,C)	19.2	16.8	18.8	18.8	19
δ(*o*-Ph)	124.7	124.9	124.8	124.7	125.8
^3J(P,C)	14.1	14.2	11.9	12.1	12.5
δ(*m*-Ph)	128.3	128.3	128.4	128.1	129.0
δ(*p*-Ph)	117.9	120.2	120.5	121.3	125.7
^{31}P{^{1}H}:					
δ(P)	82.5	76.6	80.6	87.5	74.7

products [19]. In analogy to this reaction we combined [(thf)$_4$Ca{P(H)Si*i*Pr$_3$}$_2$] [20], [(thf)$_4$Sr{P(H)Si*i*Pr$_3$}$_2$] [21], and [(thf)$_5$Ba$_2${P(H)Si*i*Pr$_3$}$_4$] [22] with diphenylbutadiyne in THF solution (Scheme 2).

The reaction of [(thf)$_4$Ca{P(H)Si*i*Pr$_3$}$_2$] with diphenylbutadiyne in an equimolar ratio in THF was followed up by ^{31}P{^{1}H} NMR spectroscopy. Besides the phospholides other resonances were observed. The H atoms at the phospholide ring stem from the starting phosphanides because a reaction in deuterated solvents also gave H substitution, and no deuterium atoms were bound at the phospholide. Excess of diphenylbutadiyne gave similar yields and a similar product distribution. These observations are in agreement with a mechanism already proposed elsewhere for the synthesis of the homologous calcium 2,5-diphenylarsolides [19]. A key step is the intermolecular exchange of a P-bound hydrogen atom by a triisopropylsilyl group because only the H atoms seem to be able to migrate intramolecularly.

NMR spectroscopy

The NMR parameters of the metal complexes **2** to **5** are compared in Table 1 with the data of the analogous ytterbium compound [(thf)$_2$Yb(PC$_4$H$_2$-2,5-Ph$_2$)$_2$] (**C**) [23]. Even though the metal atoms exhibit comparable coordination spheres, the NMR data of monovalent potassium deviate slightly from those of the divalent alkaline earth metals and ytterbium. The chemical shift δ(^{31}P{^{1}H}) of the potassium derivative **2** is similar to the value of Sr complex **4**. However, this observation is not a general trend. The ^{1}H NMR data of **2** differ significantly to those of the phospholides of the divalent metals. The carbon atoms of the phospholide ring of **2** are shifted towards lower field showing larger coupling constants to the phosphorus atom.

Molecular structures

The 2,5-diphenylphospholides of potassium (**2**), calcium (**3**), and strontium (**4**) crystallize from concentrated THF solutions as bis(tetrahydrofuran) complexes. Molecular structure and numbering scheme of the potassium derivative [(thf)$_2$K(μ-η^5,η^5-PC$_4$H$_2$-2,5-Ph$_2$)]$_\infty$ (**2**) are shown in Fig. 1. This compound

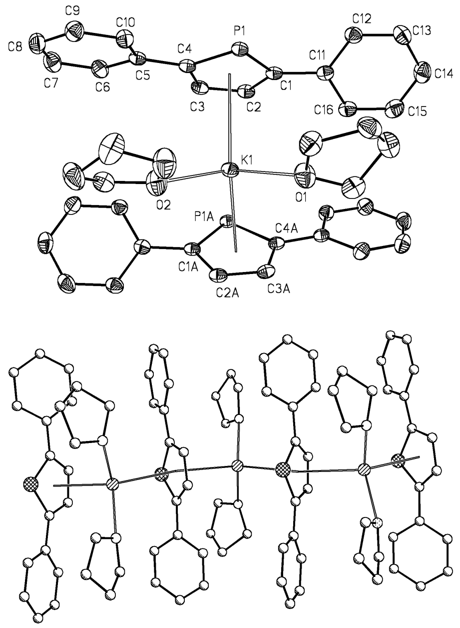


Fig. 1. Molecular structure and numbering scheme of [(thf)$_2$K(PC$_4$H$_2$-2,5-Ph$_2$)]$_\infty$ (**2**) (at the top). The displacement ellipsoids represent a probability of 40 %, H atoms are omitted for clarity reasons. Symmetry-related atoms ($-x+1/2$, $y-1/2$, $-z+1/2$) are marked with an "A". Selected bond lengths (pm): K1–C1 307.2(2), K1–C2 310.4(2), K1–C3 323.1(2), K1–C4 331.9(2), K1–P1 330.47(6), K1–O1 265.4(2), K1–O2 268.4(2), K1–C1A 319.5(2), K1–C2A 312.3(2), K1–C3A 314.3(2), K1–C4A 321.8(2), K1–P1A 334.89(7), P1–C1 176.9(2), P1–C4 177.8(2), C1–C2 140.4(3), C2–C3 138.8(3), C3–C4 140.6(3). Angles (deg): C1–P1–C4 90.57(9), P1–C1–C2 111.2(2), C1–C2–C3 113.6(2), C2–C3–C4 113.9(2), C3–C4–P1 110.7(2). At the bottom the chain structure is shown, atoms are drawn with arbitrary radii.

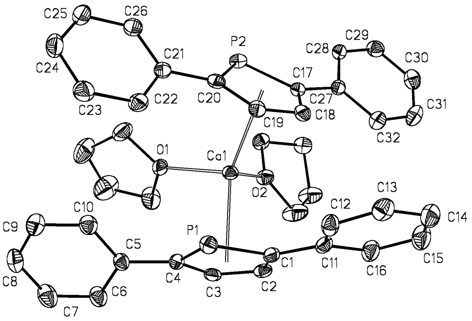


Fig. 2. Molecular structure and numbering scheme of $[(\mathrm{thf})_2\mathrm{Ca}(\mathrm{PC_4H_2}\text{-}2,5\text{-}\mathrm{Ph_2})_2]$ (**3**). The displacement ellipsoids represent a probability of 40 %. Hydrogen atoms are not shown. Selected bond lengths (pm): Ca1–O1 235.7(2), Ca1–O2 235.6(2), Ca1–P1 299.5(1), Ca1–P2 298.8(1), Ca1–C1 282.2(3), Ca1–C2 274.9(3), Ca1–C3 277.4(3), Ca1–C4 283.7(3), Ca1–C17 284.7(3), Ca1–C18 280.8(3), Ca1–C19 280.1(3), Ca1–C20 283.1(3), P1–C1 177.6(3), P1–C4 177.9(3), C1–C2 140.6(4), C2–C3 139.8(4), C3–C4 140.3(4), P2–C17 177.1(3), P2–C20 177.7(3), C17–C18 140.7(4), C18–C19 138.0(4), C19–C20 140.6(4). Angles (deg): C1–P1–C4 91.2(2), P1–C1–C2 110.1(3), C1–C2–C3 114.4(3), C2–C3–C4 113.5(3), C3–C4–P1 110.7(3), C17–P2–C20 90.4(2), P2–C17–C18 111.1(2), C17–C18–C19 113.7(3), C18–C19–C20 113.9(3), C19–C20–P2 110.8(3).

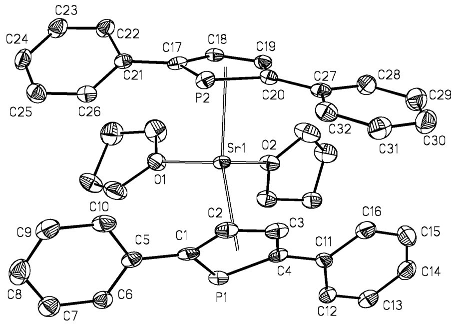


Fig. 3. Molecular structure and numbering scheme of $[(\mathrm{thf})_2\mathrm{Sr}(\mathrm{PC_4H_2}\text{-}2,5\text{-}\mathrm{Ph_2})_2]$ (**4**). The displacement ellipsoids represent a probability of 40 %. H atoms are omitted for clarity reasons. Selected bond lengths (pm): Sr1–O1 248.6(4), Sr1–O2 249.9(3), Sr1–P1 310.4(2), Sr1–P2 309.3(2), Sr1–C1 297.5(5), Sr1–C2 293.8(5), Sr1–C3 292.5(5), Sr1–C4 294.9(5), Sr1–C17 295.9(5), Sr1–C18 293.1(5), Sr1–C19 290.8(5), Sr1–C20 292.2(5), P1–C1 177.7(6), P1–C4 176.4(6), C1–C2 139.9(8), C2–C3 136.2(8), C3–C4 140.8(7), P2–C17 178.0(5), P2–C20 177.7(5), C17–C18 140.0(7), C18–C19 138.4(7), C19–C20 139.6(7). Angles (deg): C1–P1–C4 90.6(3), P1–C1–C2 109.9(4), C1–C2–C3 115.2(6), C2–C3–C4 113.3(6), C3–C4–P1 111.0(4), C17–P2–C20 90.3(2), P2–C17–C18 110.7(4), C17–C18–C19 113.9(4), C18–C19–C20 114.2(5), C19–C20–P2 110.8(4).

forms a chain-like structure with μ-η^5,η^5-bridging phospholide anions. Additional coordination of two THF molecules leads to a slight bending at the potassium atoms.

The K1–P1 distances with an average value of 332.7 pm are larger than in coligand-free $[\mathrm{K(PC_4\text{-}2,3,4,5\text{-}Et_4)}]_\infty$ (K–P 320.4 pm [24]) with a linear chain structure. Slightly enhanced but still smaller K–P distances were observed for the doubly negative anion [trans-bis{μ-η^5,η^5-2,2′-bis(3,4-dimethyl-5-phenylphospholyl)} bis{(tetrahydrofuran-*O*)potassium}] (K–P 326.0 pm [25]). The –I effect of the aryl groups in 2,5-positions of the phospholide leads to a partial reduction of anionic charge of the phospholide ring. The K–P distances depend on the number of ligands; addition of one or two THF molecules leads to enhanced K–P distances.

The alkaline earth metal derivatives **3** and **4** show a molecular structure of the type $[(\mathrm{thf})_2\mathrm{M}(\eta^5\text{-}\mathrm{PC_4H_2}\text{-}2,5\text{-}\mathrm{Ph_2})_2]$ (M = Ca (**3**), Sr (**4**)). The environment of these metal atoms is quite similar to the coordination sphere of the potassium atom in **2**. Molecular structures and numbering schemes of **3** and **4** are displayed in Figs. 2 and 3, respectively. The strontium derivative crystallizes isotypically to the ytterbium analog [26]. The asymmetric units of **3** and **4** contain two very similar molecules and therefore, the discussion and the illustrations are limited to one molecule.

Phospholides are able to coordinate *via* the soft π system (η^5 coordination) or *via* the lone pair at the phosphorus atom (η^1 coordination, formation of an M–P σ bond). For substituted 1,1′-diphosphacalcocenes (calcium diphospholides) η^5 coordination of the arene as well as σ-bonded phospholide anions are known and structurally characterized. Thus far, alkyl substituted phospholides show a preferred η^5 coordination to the alkaline earth metal cations, as observed for 3,4-dimethyl-2,5-bis(trimethylsilyl)phospholide (average Ca–P 292.3 pm [26]) and 2,3,4,5-tetraethylphospholides (average Ca–P 296.4 pm [27]). Aryl substitution as in the 2,5-diphenyl-3,4-bis(trimethylsilyl)phospholide anion leads to an η^1-*P*-bound phospholide anion (306.8 pm [18]).

Due to the similarity of the environments of the metal atoms selected structural parameters of **2** to **4** (average values) are summarized in Table 2. The anions show an η^5 coordination to the metal atoms with M–P distances resembling the size of the cations (radii of $\mathrm{K^+}$: 152, $\mathrm{Ca^{2+}}$: 114, $\mathrm{Sr^{2+}}$: 132, and $\mathrm{Yb^{2+}}$: 116 pm [28]). The larger potassium cation offers more space to the neutral THF coligands leading to a larger O1–K1–O2 angle.

Table 2. Comparison of average structural parameters of $[(thf)_2K(PC_4H_2\text{-}2,5\text{-}Ph_2)]_\infty$ (**2**), $[(thf)_2Ca(PC_4H_2\text{-}2,5\text{-}Ph_2)_2]$ (**3**), $[(thf)_2Sr(PC_4H_2\text{-}2,5\text{-}Ph_2)_2]$ (**4**), and $[(thf)_2Yb(PC_4H_2\text{-}2,5\text{-}Ph_2)_2]$ (**C**) [23] (bond lengths and cation radii $r(M^{n+})$ in pm, angles in deg).

	2	**3**	**4**	**C**
M	K	Ca	Sr	Yb
$r(M^{n+})$	152	114	132	116
M–O	266.9	235.7	249.3	239.5
M–P	332.7	299.1	309.9	297.3
M–C1,4	320.1	283.4	295.1	282.4
M–C2,3	315.0	278.3	292.6	280.0
P–C1,4	177.4	177.6	177.5	177.5
C1,3–C2,4	140.5	140.6	140.1	139.9
C2–C3	138.8	138.9	137.3	139.3
C1,4–C_{Ph}	147.2	146.5	147.1	
P–M–P	125.0	126.6	127.4	
Cent–M–Cent	125.4	128.9	126.4	
O1–M–O2	93.6	81.3	81.7	82.2
C1–P–C4	90.6	91.2	90.6	90.3

In all these complexes **2** to **4** charge delocalization within the phospholide is observed which can easily be recognized by the alignment of the endocyclic C–C and C=C bond lengths. In 1,2,5-triphenylphosphole C–C and C=C bond lengths of 144.0 and 135.0 pm are observed [29]. In addition, the P–C bonds to the pyramidally coordinated phosphorus atom show an average value of 182.2 pm. In comparison to neutral 1,2,5-triphenylphosphole a far-reaching charge delocalization is realized in the 2,5-diphenylphospholid anions of **2**, **3**, and **4** leading to P–C multiple bonds and rather similar endocyclic C–C bond lengths. The charge delocalization within the phospholides often led to the discussion of aromaticity in these phosphaarene anions. Several criteria support that the aromaticity of the phospholide anions is only slightly reduced in comparison to the carbon analog (see discussions in [30]).

Summary

Due to the fact that P–C bonds are broken by elemental potassium, the reduction of 1,4-diphenyl-NUPHOS (**1**) is an irreversible reaction. The reduction of **1** yields bis(tetrahydrofuran-*O*)potassium bis(2,5-diphenylphospholide) (**2**) which crystallizes with a chain structure (1D polymeric structure). The metathesis reactions with the alkaline earth metal diiodides of calcium, strontium, and barium leads to the formation of the corresponding derivatives. Another access route to these bis(tetrahydrofuran-*O*)alkaline earth metal bis(2,5-diphenylphospholides) [Ca (**3**), Sr (**4**), and Ba (**5**)] starts from the addition of a metal-phosphorus bond of $M\{P(H)Si\textit{i}Pr_3\}_2$ to a C≡C triple bond of diphenylbutadiyne. Subsequent H migration and intermolecular trialkylsilyl/hydrogen exchange reactions yield the 2,5-diphenylphospholides of these alkaline earth metals.

The 2,5-diphenylphospholide anions bind in an η^5 fashion to the metal centers. This observation was surprising because the rather similar 2,5-diphenyl-3,4-bis(trimethylsilyl)phospholide anions form M–P σ bonds (η^1 coordination). All phospholide anions with alkyl substituents show a side-on coordination behavior. The molecular structures of **3** and **4** clearly demonstrate that also aryl-substituted phospholides prefer η^5 coordination with the bulky 2,5-diphenyl-3,4-bis(trimethylsilyl)phospholide anions remaining an exception.

Experimental Section

General: All manipulations were carried out in an argon atmosphere under anaerobic conditions. The compounds are extremely moisture-sensitive and lose coordinated THF once isolated. Prior to use, all solvents were thoroughly dried and distilled in an argon atmosphere. NMR spectra were recorded on Bruker AC 400 MHz and Jeol EX 400 MHz spectrometers. IR spectra were measured at Nujol suspensions between KBr windows. 1,4-Diphenyl-NUPHOS [8], $[(thf)_4M\{P(SiMe_3)_2\}_2]$ of calcium [20] and strontium [21] as well as $[(thf)_5Ba_2\{P(H)Si\textit{i}Pr_3\}_4]$ [22] were prepared according to known procedures. Potassium 2,5-diphenylphospholide is also accessible according to known protocols from potassium and 1,2,5-triphenylphosphole [16, 31], and our physical data are in agreement with published data. The elemental analyses suffer from the moisture and air sensitivity of these phospholides. In addition, low carbon values may result from carbonate formation during combustion despite addition of V_2O_5. NMR values are listed in Table 1.

Bis(tetrahydrofuran-O)potassium bis(2,5-diphenylphospholide) (2)

1,4-Diphenyl-NUPHOS (171 mg, 0.3 mmol) was dissolved in 7 mL of THF. At r. t. an excess of potassium (pea-like piece, freed from the oxide layer) was added. Within a few minutes the reaction mixture turned red-brown. After 3 h unreacted potassium was removed. The volume of the filtrate was reduced to a third of the original volume. Storage at −20 °C for 4 d led to crystallization of colorless **2**. – Dec. above 275 °C. – ^{1}H NMR (400.00 MHz, [D$_8$]THF): δ = 6.36 (t, $^3J_{HH}$ = 7.2 Hz, Ph, *p*-H), 6.71 (m, phospholide H3 and H4), 7.41 (m, Ph, *m*-H); 7.68 (d, $^3J_{HH}$ = 8.0 Hz, Ph, *o*-H); 1.78 and 3.62 (THF). – $^{13}C\{^1H\}$ NMR (100 MHz, [D$_8$]THF): δ = 117.9 (s, Ph, *p*-C); 124.7 (d, $^3J_{PC}$ = 14.1 Hz, Ph, *o*-C); 127.3 (d, $^2J_{PC}$ = 5.6 Hz, phospholide C3 and C4); 128.3 (s, Ph, *m*-C); 129.2 (d, $^2J_{PC}$ = 19.2 Hz, Ph, *i*-C); 159.2 (d, $^1J_{PC}$ = 53.7 Hz, phospholide C2 and C5), 25.5 and 67.3 (THF). – $^{31}P\{^1H\}$ NMR (81.00 MHz, [D$_8$]THF): δ = 82.5 (s).

Synthesis of the bis(tetrahydrofuran-O)alkaline earth metal bis(2,5-diphenylphospholides)

Procedure A

Anhydrous CaI$_2$, SrI$_2$, and BaI$_2$, respectively, were given to a solution of a stoichiometric amount of bis(tetrahydrofuran-*O*)potassium bis(2,5-diphenylphospholide) (**2**) in [D$_8$]THF. According to the $^{31}P\{^1H\}$ NMR spectra a quantitative conversion was achieved.

Procedure B

Toluene (15 mL) was filled into a V-shaped Schlenk tube with the two arms separated by a GIII frit. Thereafter, 0.24 g of diphenylbutadiyne (1.2 mmol, dissolved in 3 mL of toluene) was given into one side, a solution of 1.2 mmol of M{P(H)Si*i*Pr$_3$}$_2$ in 3 mL of THF was layered in the other. The solution turned brown, and the reaction was controlled *via* $^{31}P\{^1H\}$ NMR spectroscopy. Within one week all starting phosphanides had reacted, and the brown reaction mixture was poured into a common Schlenk flask. The volume was reduced to a third of the original volume. Storage at 4 °C led to precipitation of colorless crystals of **3** (M = Ca, 0.37 g, 0.57 mmol, 48 %, based on starting Ca component), **4** (M = Sr, 0.49 g, 0.70 mmol, 44 %, based on starting Sr component), and **5** (M = Ba, 0.26 g, 0.34 mmol, 28 %, based on starting Ba component), respectively. Larger amounts of diphenylbutadiyne do not give higher yields based on the metal phosphanides.

Characterization and physical properties

*Bis(tetrahydrofuran-O)calcium bis(2,5-diphenylphospholide) (**3**)*

Dec. above 275 °C. – ^{1}H NMR (399.79 MHz, [D$_8$]THF): δ = 7.06 (m, Ph, *p*-H); 7.23 (m, Ph, *m*-H); 7.30 (m, phospholide H3 and H4), 7.67 (m, Ph, *o*-H), 1.77 and 3.62 (THF). – $^{13}C\{^1H\}$ NMR (100.54 MHz, [D$_8$]THF): δ = 120.2 (s, Ph, *p*-C); 124.9 (d, $^3J_{PC}$ = 14.2 Hz, Ph, *o*-C); 125.1 (s, phospholide C3 and C4); 128.21 (s, Ph, *m*-C); 140.6 (d, $^2J_{PC}$ = 16.8 Hz, Ph, *i*-C); 151.6 (d, $^1J_{PC}$ = 44.8 Hz, phospholide C2 and C5), 25.5 and 67.3 (THF). – $^{31}P\{^1H\}$ NMR (161.84 MHz, [D$_8$]THF): δ = 76.6 (s). – IR (cm^{-1}): ν = 1696 vw, 1591 s, 1571 w, 1560 vw, 1503 m, 1491 m, 1456 w, 1446 m, 1423 w, 1333 vw, 1303 vw, 1267 m, 1190 sh, 1180 w, 1175 sh, 1155 w, 1081 w, 1071 m, 1021 m, 1000 w, 983 vw, 964 vw, 939 vw, 906 w, 876 m, 860 sh, 841 w, 825 vw, 799 s, 758 vs, 729 m, 695 vs, 677 w, 595 vw, 568 w, 475 w, 461 m. – CaP$_2$C$_{40}$H$_{40}$O$_2$ (654.74): calcd. C 73.37, H 6.16; found C 72.37, H 6.55.

*Bis(tetrahydrofuran-O)strontium bis(2,5-diphenylphospholide) (**4**)*

Dec. above 275 °C. – ^{1}H NMR (399.79 MHz, [D$_8$]THF): δ = 7.11 (m, Ph, *p*-H); 7.23 (m, Ph, *m*-H); 7.27 (m, phospholide H3 and H4), 7.64 (m, Ph, *o*-H), 1.72 and 3.58 (THF). – $^{13}C\{^1H\}$ NMR (100.54 MHz, [D$_8$]THF): δ = 120.5 (s, Ph, *p*-C); 124.8 (d, $^3J_{PC}$) = 11.9 Hz, Ph, *o*-C); 124.9 (s, phospholide C3 and C4); 128.4 (s, Ph, *m*-C); 140.5 (d, $^2J_{PC}$ = 18.8 Hz, Ph, *i*-C); 152.8 (d, $^1J_{PC}$ = 45.3 Hz, phospholide C2 and C5), 23.6 and 65.4 (THF). – $^{31}P\{^1H\}$ NMR (161.84 MHz, [D$_8$]THF): δ = 80.6 (s). – IR (cm^{-1}): ν = 3085 m, 3055 s, 3033 s, 1949 w, 1876 w, 1810 w, 1744 w, 1667 vw, 1616 vw, 1592 vs, 1571 m, 1502 vs, 1493 sh, 1446 s, 1432 vw, 1430 w, 1391 vw, 1369 vw, 1342 sh, 1335 w, 1304 w, 1296 sh, 1266 s, 1212 w, 1194 w, 1183 w, 1169 w, 1156 w, 1102 vw, 1081 m, 1071 m, 1029 vs, 1000 w, 983 vw, 963 w, 941 w, 905 s, 878 s, 849 sh, 842 sh, 796 vs, 757 vs, 728 s, 685 vs, 677 w, 667 w, 620 vw, 609 vw, 595 vw, 568 w, 519 vw, 475 w, 463 s, 429 vw, 409 vw, 358 vw, 350 vw. – SrP$_2$C$_{40}$H$_{40}$O$_2$ (702.28): calcd. C 68.41, H 5.74; found C 68.23, H 5.83.

*Bis(tetrahydrofuran-O)barium bis(2,5-diphenylphospholide) (**5**)*

Dec. above 188 °C. – ^{1}H NMR (399.79 MHz, [D$_8$]THF): δ = 6.99 (m, Ph, *p*-H); 7.19 (m, Ph, *m*-H); 7.05 (m, phospholide H3 and H4), 7.62 (m, Ph, *o*-H), 1.72 and 3.57 (THF). – $^{13}C\{^1H\}$ NMR (100.54 MHz, [D$_8$]THF): δ = 121.3 (s, Ph, *p*-C); 124.7 (d, $^3J_{PC}$ = 12.1 Hz, Ph, *o*-C); 124.3 (s, phospholide C3 and C4); 128.1 (s, Ph, *m*-C); 141.3 (d, $^2J_{PC}$ = 18.8 Hz, Ph, *i*-C); 153.0 (d, $^1J_{PC}$ = 40.7 Hz, phospholide C2 and C5), 24.4 and 66.5 (THF). – $^{31}P\{^1H\}$ NMR (161.84 MHz, [D$_8$]THF): δ = 87.5 (s). – IR (cm^{-1}): ν = 1591 m, 1572 vw, 1501 w, 1491 w, 1445 w, 1433 vw, 1370 vw, 1362 vw, 1321 vw, 1300 vw, 1264 w, 1157 w, 1101 vw, 1067 w, 1057 w, 1032 w, 998 vw, 986 vw, 967 vw, 929 vw, 904 vw, 881vw, 843 vw, 800 vw, 786 vw, 756 vs, 728 vw, 693 m, 677 vw, 595 vw, 530 vw, 463 vw. – BaP$_2$C$_{40}$H$_{40}$O$_2$ (751.99): calcd. C 63.89, H 5.36; found C 60.23, H 5.27.

Structure Determinations

The intensity data for the compounds were collected on a Nonius KappaCCD diffractometer (**2**) and on a Bruker Smart CCD camera system at fixed 2θ (**3** and **4**), using graphite-monochromatized MoK_α radiation. Data were corrected for Lorentz and polarization effects and for absorption effects only for **3** and **4** [32 – 35].

The structures were solved by Direct Methods (SHELXS [36]) and refined by full-matrix least-squares techniques

Table 3. Crystal data and refinement details for the X-ray crystal structure determinations of the compounds **2**, **3**, and **4**.

Compound	**2**	**3**	**4**
Formula	$C_{24}H_{28}KO_2P$	$C_{40}H_{40}CaO_2P_2$	$C_{40}H_{40}O_2P_2Sr$
F_w, g mol^{-1}	418.53	654.74	702.28
T, K	−90(2)	−80(2)	−80(2)
Crystal system	monoclinic	triclinic	monoclinic
Space group	$P2_1/n$	$P\bar{1}$	$P2_1/n$
a, Å	8.8945(2)	13.2851(12)	16.3950(11)
b, Å	10.3727(3)	16.7298(17)	17.6079(12)
c, Å	24.5004(8)	16.8433(16)	24.0371(16)
α, deg	90	86.035(2)	90
β, deg	91.510(2)	68.143(2)	93.810(2)
γ, deg	90	82.432(2)	90
V, Å^3	2259.62(11)	3443.4(6)	6923.7(8)
Z	4	4	8
ρ, g cm^{-3}	1.23	1.26	1.35
μ, mm^{-1}	3.2	3.1	16.8
Absorption method	none	multi-scan	multi-scan
Measured data	21735	20249	40793
Unique data / R_{int}	5183 / 0.0641	10796 / 0.0414	12035 / 0.1005
Data with $I \geq 2\sigma(I)$	3757	6040	7676
$R1$ $[I \geq 2\sigma(I)]^a$	0.0455	0.0418	0.0671
$wR2$ (all data, on F^2)^a	0.1232	0.1042	0.1279
S (GoF)^b	1.017	0.883	1.071
$\Delta\rho_{fin}$ (max/min), e Å^{-3}	0.716 / −0.363	0.443 / −0.243	0.539 / −0.496
CCDC No.	745744	745745	745746

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

against $F_o{}^2$ (SHELXL-97 [37]). All hydrogen atoms were included at calculated positions with fixed thermal parameters. All non-disordered, non-hydrogen atoms were refined anisotropically [37]. Crystallographic data as well as structure solution and refinement details are summarized in Table 3. XP (Siemens Analytical X-ray Instruments, Inc.) was used for structure representations.

CCDC 745744 (**2**), 745745 (**3**), and 745746 (**4**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre *via* www.ccdc.cam.ac.uk/data_request/cif.

Acknowledgements

We thank the Deutsche Forschungsgemeinschaft (DFG, Bonn-Bad Godesberg, Germany) and the Fonds der Chemischen Industrie (Frankfurt/Main, Germany) for generous financial support. In addition, R. Kretschmer thanks the Hans-Böckler-Stiftung for a scholarship, and S. Krieck is very grateful to the Verband der Chemischen Industrie (VCI/FCI) for a generous Ph.D. grant.

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