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Synthesis of alkaline earth metal bis(2-phosphaethynolates)

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Dedicated to Professor François Mathey on the occasion of his 60th birthday

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Abstract

The reaction of dimethylcarbonate with magnesium bis(triisopropylsilyl phosphanide) or the alkaline earth metal bis-[bis(trimethylsilyl)phosphanide] in 1,2-dimethoxyethane yields the corresponding bis(2-phosphaethynolate) of magnesium (**1**), calcium (**2**), strontium (**3**) and barium (**4**). These compounds decompose upon isolation and have to be stored in an etheral solution at low temperatures. The structure of $(dme)_3Ca(O–C≡P)_2$ shows bent Ca–O–C moieties and rather long C≡P triple bonds of 1.575 Å. In order to ensure a quantitative reaction an excess of dimethylcarbonate has to be used. For the strontium derivative a side reaction of a 1:3 stoichiometry of $M[P(SiMe_3)_2]_2$ to $(MeO)_2CO$ gave a tridentate ligand which bridges two strontium atoms. The molecular structure of dimeric $(dme)_2Sr\{OC[PC(O)OMe]_2\}$ (**5**) showed the delocalization of the anionic charge within the O–C–P–C–P–C–O fragment. © 2002 Elsevier Science B.V. All rights reserved.

Keywords: Alkaline earth metal bis(2-phosphaethynolates); Phosphaalkynes; Triple bonds; Delocalization

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1. Introduction

Several years ago the first report [1] of a 2-phosphaethynolate $P≡C–O^-$ gained much attention because this anion is isoelectronic to small molecules such as O=C=S and F–C≡P as well as the thiocyanate anion $S=C=N^-$ [2]. An amino substituted phosphaalkyne was even published 12 years ago [3]. These small anions are not only of interest in the field of the pseudo halides [2] but also for investigations regarding multiple bonds between carbon and the main group elements of the third and higher periods. In this context, the chemistry of the alkyl-2-phosphaethynes was explored extensively [4], also theoretical investigations on coligand-free metal 2-phosphaethynolates were performed [5–7].

The DME complex of Li–O–C≡P is available by the reaction of lithium bis(trimethylsilyl)phosphanide with dimethylcarbonate in 1,2-dimethoxyethane [1] whereas the use of $^{i}Pr_3SiP(SiMe_3)_2$ as a synthon led to oily triisopropylsiloxy 2-phosphaethyne [8]. Even though the first report appeared nearly ten years ago [1], there are only sporadic investigations regarding the chemistry of these 2-phosphaethynolate anions in contrast to the widely explored reaction behavior of the alkyl-2-phosphaalkynes [4,9]. The metathesis reaction of Li–O–C≡P with $(\eta^5\text{-}C_5R_5)(CO)_2FeBr$ yielded 1,3-diferrio-1,3-diphosphetane-2,4-diones as a red solid [10]. The oxidation of Li–O–C≡P with iodine or SO_2 gave a cage compound consisting of four phosphaalkyne units [11] whereas the transformation to $[Li(DME)_3]^+[S–C≡P]^-$ was succeeded by the reaction of $(DME)_2Li–O–C≡P$ with carbon disulfide [12].

2. Results and discussion

In order to compare the reactivity of the bis(trimethylsilyl)phosphanides of lithium and the alkaline earth metals [13] the alkaline earth metal bis(2-phosphaethynolates) were prepared. Magnesium triisopropylsilylphosphanediide reacts with dimethylcarbonate to $Mg(O–C≡P)_2$ (**1**), magnesium methanolate and $MeO–Si^{i}Pr_3$. The reaction of alkaline earth metal bis[bis(trimethylsilyl)phosphanides] with dimethylcar-

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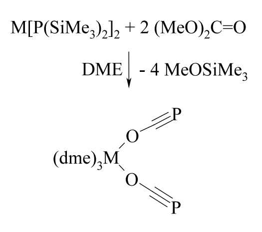
bonate in THF or 1,2-dimethoxyethane (DME) gave the corresponding magnesium (**1**), calcium (**2**), strontium (**3**) and barium bis(2-phosphaethynolates) (**4**) under elimination of methyl trimethylsilylether according to 1. A double 1,3-trimethylsilyl shift from the phosphorus atom to the methoxy groups gives the P≡C–O moiety. These colorless compounds decompose slowly in etheral solutions and rapidly under vacuum or in hydrocarbon solutions. Therefore, the characterization of these compounds was limited to NMR experiments. The complexation of calcium bis(2-phosphaethynolate) (**2**) by three DME coligands led to a slight enhancement in stability and therefore, we were able to isolate crystalline **2** and to solve its molecular structure.



(1)

In order to guarantee a quantitative reaction an excess of dimethylcarbonate was used, because this compound is volatile and easily removed after complete conversion. However, in the case of strontium bis(2-phosphaethynolate) (**3**), a molecule with a higher content of dimethylcarbonate was formed according to 2 and isolated in a very low yield. Due to the poor crystallization behavior of **3**, colorless crystals of dimeric bis(1,2-dimethoxyethane-*O*,*O′*)strontium 2,6-bis(methoxy)-3,5-diphospha-1,7-dioxaheptatrienide-4-olate (**5**) were obtained and the molecular structure determined by X-ray diffraction methods.

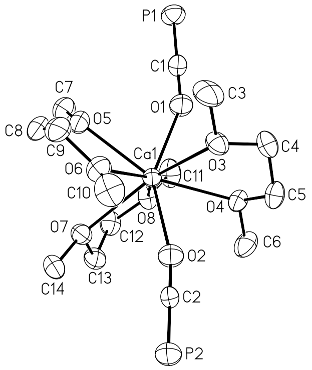


Fig. 1. Molecular structure and numbering scheme of **2**. The ellipsoids represent a probability of 40%. All hydrogen atoms are neglected for clarity reasons. Selected bond lengths (Å): Ca1–O1 2.358(2), Ca1–O2 2.335(2), Ca1–O3 2.478(2), Ca1–O4 2.536(2), Ca1–O5 2.480(2), Ca1–O6 2.463(2), Ca1–O7 2.554(2), Ca1–O8 2.438(2), O1–C1 1.207(3), P1–C1 1.575(2), O2–C2 1.199(3), P2–C2 1.575(2); bond angles (°): O1–Ca1–O2 147.73(7), Ca1–O1–C1 154.6(2), O1–C1–P1 179.2(2), Ca1–O2–C2 165.1(2), O2–C2–P2 179.9(3).

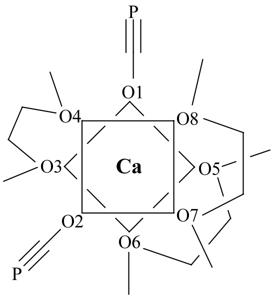
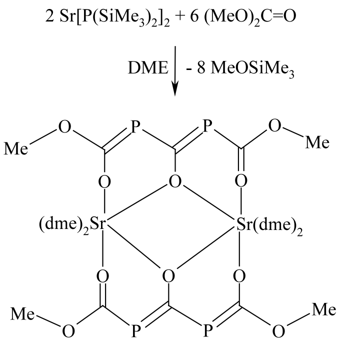


Fig. 2. Representation of the square antiprismatic coordination sphere of the calcium center of **2**.



5

(2)

All of these alkaline earth metal bis(2-phosphaethynolates) are extremely sensitive towards moisture and air. Even the loss of coordinating coligand leads to a decomposition of these compounds. Therefore, **1**–**4** were not isolated but handled under excess of solvent or mother liquor. However, at −20 °C the dimethoxyethane solutions of the alkaline earth metal bis(2-phosphaethynolates) can be stored for several weeks.

3. Molecular structures

The molecular structure of **2** is represented in Fig. 1. The calcium atom is octa-coordinate by oxygen atoms. The Ca1–O1 (2.358(2) Å) and Ca1–O2 (2.335(2) Å) bonds are shorter due to the electrostatic attraction between the dicationic center and the anions whereas the other Ca–O contacts to the DME ligands lie between 2.438(2) and 2.554(2) Å. The coordination polyhedron is best described as a square antiprism as shown in Fig. 2. Due to this symmetry the O1–Ca1–O2 angle amounts 147.73(7)°.

The Ca1–O1–C1 (154.6(2)°) as well as Ca1–O2–C2 moities (165.1(2)°) are bent as also found for the acetylides [14] and the pentacarbonyl(cyano)metallates(0) of the heavier alkaline earth metals [15]. This fact is most probably the consequence of

Table 1
Comparison of the $\delta(^{31}P\{^{1}H\})$ values as well as distinguished structural parameters of selected phosphaalkynes (neutral coligands are neglected in the compound formula)

Compound	δ ($^{31}P\{^{1}H\}$)	d (R–C) (Å)	d (C≡P) (Å)	RCP (°)	Ref.
$Ca(O–C\equiv P)_2$[a]	−369.6	1.207(3)	1.575(2)	179.2(2)	This work
$Li–O–C\equiv P$[a]	−384.2	1.198(4)	1.555(4)	178.5(3)	[1]
$Li^{+}[S–C\equiv P]^{-}$[a]	−121.3	1.620(11)	1.555(11)	178.9(7)	[12]
$H–C\equiv P$[b]	−32.0	1.0667(5)	1.540(4)	180	[16,17]
$Me–C\equiv P$[b]	−60.0	1.465(3)	1.544(4)	180	[16,18]
tBu–C≡P[b]	−69.2	1.473(5)	1.536(5)	180	[4,19]
tBu–C≡P[a]		1.470(3)	1.542(2)	179.3(2)	[20]
$^{i}Pr_2N–C\equiv P$[a]	−99.6	1.312(3)	1.552(2)	179.2(2)	[21,22]
tmp–C≡P[a,c]	−103.7	1.316(2)	1.559(2)	178.9(1)	[23]
F–C≡P[b]	−207	1.285(5)	1.541(5)	180	[24]
Cl–C≡P[b]	−116	1.635(5)	1.554(5)	180	[25,26]

[a] X-ray structure determination.
[b] Microwave spectroscopy.
[c] Tetramethylpiperidyl.

packing effects because these compounds are mainly ionic and electrostatic arguments dominate the metal–ligand interactions. The OCP anions are linear with O–C and C≡P distances of 1.20 and 1.575 Å, respectively. In Table 1 the structural parameters of selected phosphaalkynes are compared. In alkylmethylidynephosphanes undisturbed CP triple bonds are observed, whereas in compounds of the formula PCX^{-} two mesomeric forms have to be taken into account, namely the phosphaalkyne $P\equiv C–X^{-}$ as well as the cumulene system of the type $^{-}P{=}C{=}X$. The structural data indicate that the heterocumulene system contributes to the structure of the $Ca(O–C\equiv P)_2$ unit of **2**. In Table 1 a comparison of the chemical $^{31}P\{^{1}H\}$ NMR shifts as well as distinguished structural parameters of selected phosphaalkynes are given and shows that in **2** a rather long C≡P bond is observed. Furthermore, the chemical shifts of the phosphaalkynolates are detected at an extremely high field. At the low field side a value of $\delta(^{31}P) = +96$ is detected for $Me_3Si–C\equiv P$ [27].

The molecular structure of **5** and its numbering scheme are represented in Fig. 3. The strontium atoms show a coordination number of eight. The Sr–O bond lengths to the diphosphatriketonate ligand are smaller than to the ether oxygen atoms due to the smaller coordination numbers of the donor atoms and due to the electrostatic attraction. The structure of the dianionic ligand is depicted in Fig. 4. The P–C distances indicate a delocalization of the anionic charge within the fragment O3–C3–P4–C5–P6–C7–O7 which can be regarded as a 3,5-diphospha-1,7-dioxaheptatrienide. The C3–O3 as well as C7–O7 bond lengths of approximately 1.22 Å clearly indicate multiple bond character (comparison: 1.20 Å for the C–O double bond in formaldehyde, 1.34 Å for the single bond in formic acid), whereas the terminal bonds to the oxygen atoms O2 and O8 show characteristic single bond lengths of approximately 1.44 and 1.36 Å to the sp^{3} and sp^{2} hybridized carbon atoms.

Phospha-β-diketonates [28] as well as -diketones [29] show a similar delocalization of the anionic charge within an O–C–P–C–O moiety. In these compounds P–C distances of approximately 1.79 Å were observed.

The second anionic charge of **5** is located at O5 which is in a bridging position between the strontium centers. The C5–O5 distance of nearly 1.30 Å is larger than the C–O bond lengths of the 3,5-diphospha-1,7-dioxaheptatrienide backbone. This backbone is twisted and therefore, the C3–O3 and C5–O5 bonds include an angle of 34.1°, the C5–O5 and C7–O7 bonds an angle of 23.1° and finally the C3–O3 and C7–O7 bonds an angle of 57.2°.

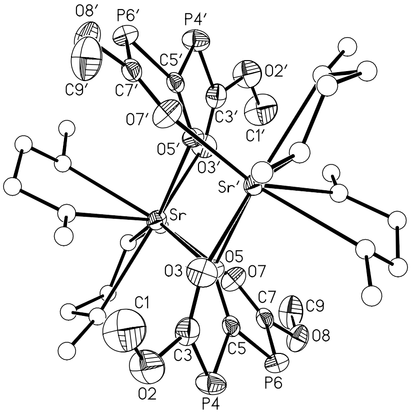


Fig. 3. Molecular structure and numbering scheme of **5**. The ellipsoids represent a probability of 40%. Atoms generated by inversion symmetry ($-x+1$, $-y$, $-z+1$) are marked with an apostrophe. The atoms of the neutral coligands are drawn with arbitrary radii, the H atoms neglected for clarity reasons. Selected bond lengths (Å): Sr–O3′ 2.492(2), Sr–O5 2.500(2), Sr–O5′ 2.541(2), Sr–O7 2.496(2), Sr–O21 2.661(2), Sr–O22 2.609(2), Sr–O51 2.663(2), Sr–O52 2.689(2); bond angles (°): Sr–O3′–C3′ 136.8(2), Sr–O7–C7 137.9(2), Sr–O5–C5 129.9(2), Sr′–O5–C5 121.0(2), Sr–O5–Sr′ 108.52(7).

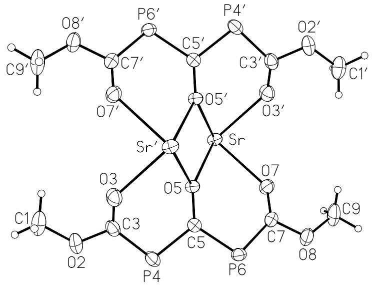


Fig. 4. Representation of the anionic ligands of **5**. The neutral coligands are neglected for clarity reasons. Selected bond lengths (Å): C1–O2 1.444(4), O2–C3 1.361(4), C3–O3 1.225(4), C3–P4 1.800(3), P4–C5 1.789(3), C5–O5 1.295(3), C5–P6 1.789(3), P6–C7 1.790(3), C7–O7 1.219(3), C7–O8 1.366(3), O8–C9 1.423(4); bond angles (°): C3–P4–C5 101.5(1), C5–P6–C7 102.6(1).

4. Conclusion

The preparation of alkaline earth metal bis(2-phosphaethynolate) succeeds in a similar way as described for the lithium derivative. However, the sensitivity with regard to the loss of coordinating solvent molecules seems to be higher than reported for Li–O–C≡P. A reason for this observation could be that the phosphaethynolate anions are very close together due to the binding to the same cation, which could favor the following reactions and hence the decomposition of **1** to **4**. We were able to characterize one of these decomposition products in the case of **5**.

5. Experimental

All experiments and manipulations were carried out under Ar. Reactions were performed by using standard Schlenk techniques and dried, thoroughly deoxygenated solvents. The starting alkaline earth metal bis[bis(trimethylsilyl)phosphanides] [13] of calcium, strontium, and barium were prepared according to literature procedures. NMR spectra were recorded in JEOL GSX270 and EX400 spectrometers. No analytical data were presented due to the failure of isolation of these compounds.

*5.1. Magnesium bis(2-phosphaethynolate) (**1**)*

Triisopropylsilylphosphane (0.90 ml, 4.0 mmol) was dissolved in 20 ml of toluene. Then 4.0 ml of a 1 molar hexane solution of dibutylmagnesium was added. To this solution 1.02 ml of dimethylcarbonate (12 mmol) was dropped at − 20 °C. The solution turned red. The quantitative conversion was monitored by NMR spectroscopy, however, an isolation of **1** failed due to decomposition after isolation (see text).

*5.2. General procedure for calcium (**2**), strontium (**3**) and barium bis(2-phosphaethynolate) (**4**)*

A solution of 0.19 mmol of $(thf)_2M[P(SiMe_3)_2]_2$ in 5 ml of 1,2-dimethoxyethane was dropped to a solution of 0.03 ml of dimethylcarbonate (0.58 mmol) in 5 ml of DME at − 20 °C. As the solution warmed to room temperature it turned red. The solution was concentrated and the precipitate was removed by filtration. At − 30 °C the calcium derivative **2** crystallized in the shape of red cuboids. These compounds could be stored in the mother liquor at − 20 °C for several weeks before a brown precipitate formed, but the isolated compounds decomposed immediately. During the storage of the DME solution of **3** a few crystals of **5** formed which were investigated by X-ray crystallography.

$^{31}P\{^1H\}$ NMR data (mixture of DME and [D$_6$]benzene, 30°C): **1** $\delta = -371.1$, **2** $\delta = -369.6$, **3** $\delta = -373.2$, **4** $\delta = -362.3$. All resonances were broad and therefore, the $^{13}C\{^1H\}$ NMR signals of the O–C≡P carbon atoms were not detected. Correct metal to phosphorus ratios were determined by elemental analysis (ICP).

5.3. X-ray structure determination

The single crystals of **2** and **5** were covered with oil [30] and mounted on a Siemens P4 and on a STOE IPDS diffractometer, respectively, with graphite monochromated Mo–K$_\alpha$ radiation ($\lambda = 0.71073$ Å). Crystallographic parameters and details of data collection are summarized in Table 2.

The structures were solved by direct methods and refined with the software packages SHELXL-93 and SHELXL-97 [32]. Neutral scattering factors were taken from Cromer and Mann [33] and for the hydrogen atoms from Stewart et al. [34]. The H-atoms were considered with a riding model under restriction of ideal symmetry at the corresponding atom.

6. Supplementary material

Crystallographic data for the structural analysis have been deposited with the Cambridge Crystallographic Data Centre, CCDC nos. 165906 and 166019 for compounds **2** and **5**, respectively. Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (Fax: + 44-1223-336033; e-mail: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk).

Table 2
Crystal data and structure refinement parameters for **2** and **5**

Compound	**2**	**5**
Empirical formula	$C_{14}H_{30}CaO_8P_2$	$C_{26}H_{52}O_{18}P_4Sr_2$
Formula weight (g mol^{-1})	428.40	951.80
T (K)	193(2)	200(2)
Space group [31]	$P2_1$ (No. 4)	$Pbca$ (No. 61)
Unit cell dimensions		
a (Å)	8.4642(6)	18.792(1)
b (Å)	10.3889(8)	15.0382(9)
c (Å)	13.087(1)	14.9367(7)
β (°)	94.516(1)	90
V (Å^3)	1147.2(2)	4221.1(4)
Z	2	4
ρ_{calcd} (g cm^{-3})	1.240	1.498
λ (Å)	0.71073	0.71073
μ (cm^{-1})	0.445	2.744
Absorption correction	SADABS	Numerical
Min/max transmission	0.700/0.862	0.634/0.664
No. of data collected	6661	25503
No. of independent data (R_{int})	4393 (0.0195)	3297 (0.0621)
Flack parameter	0.02(3)	
Goodness-of-fits on F^2 [a]	1.033	0.861
wR_2 indices [on F^2, all data] [b]	0.0802	0.0548
R_1 [on F^2, $I > 2\sigma(I)$]	0.0333	0.0274
Residual density (e Å^{-3})	0.219/−0.200	0.283/−0.297
CCDC number	165906	166019

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

[b] 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 $w^{-1} = \sigma^2(F_o^2) + (aP)^2$.

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