Isoelectronic caesium compounds: the triphosphenide Cs[tBu$_3$SiPPPSitBu$_3$] and the enolate Cs[OCH=CH$_2$]†‡

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The caesium triphosphenide Cs[tBu$_3$SiPPPSitBu$_3$] was accessible from the reaction of CsF with the sodium triphosphenide Na[tBu$_3$SiPPPSitBu$_3$] in tetrahydrofuran at room temperature. In contrast to the preparation of tetrahydrofuran-solvated silanides M[SitBu$_3$] (M = Li, Na, K), our efforts to synthesize the caesium silanide Cs[SitBu$_3$] as a tetrahydrofuran complex failed. When tBu$_3$SiBr was treated with an excess of caesium metal in tetrahydrofuran at room temperature, the caesium enolate Cs[OCH=CH$_2$] and the supersilane tBu$_3$SiH formed rather than the silanide Cs[SitBu$_3$]. X-Ray quality crystals of the enolate Cs[OCH=CH$_2$] (orthorhombic, *Pnma*) were obtained from tetrahydrofuran at ambient temperature. In contrast to the structures of its homologues M[tBu$_3$SiPPPSitBu$_3$] (M = Na, K), the caesium triphosphenide Cs[tBu$_3$SiPPPSitBu$_3$] features a polymer in the solid state (orthorhombic, *Cmcm*).

Introduction

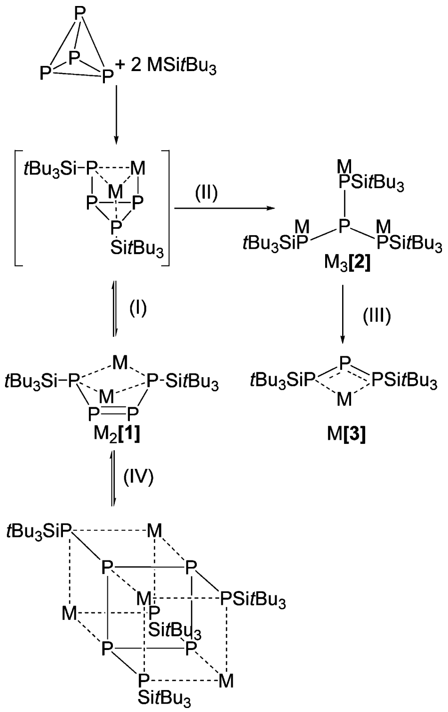
Over the past two decades, phosphides have gained prominence in wide areas of application. However, up to now only polyphosphidic Zintl ions have been found to play an important role in materials science. These Zintl ions are synthesized generally at high temperatures by solid-state reactions.[1]

The first studied phosphanides which consist of discrete molecules with organic or organosilyl substituents on the P-centres were alkali metal, alkaline earth metal or transition metal monophosphanides, M[PHR] and M[PR$_2$].[2] Contrary to the preparation of polyphosphidic Zintl ions, the monophosphanides have been synthesized almost under mild conditions. In contrast to the well-established monophosphanides only a few monophosphanediide and oligophosphanide derivatives, M$_2$[PR][3] and M$_x$[P$_m$R$_m$][4] ($m > 2$), have been fully characterized.

The purpose of this paper is to report about a phosphorus analogue of the allyl anion (triphosphenide).

Recently we have reported on the reaction of P$_4$ with the silanides M[SitBu$_3$] (M = Li, Na) and Na[SiPhtBu$_2$] in a 1 : 3 stoichiometry, which cleanly led to the formation of the tetraphosphides M$_3$[P$_4$(SitBu$_3$)$_3$] (M = Li, Na) and Na$_3$[P$_4$(SiPhtBu$_2$)$_3$], respectively, as shown in Scheme 1. However, the tetraphosphides M$_3$[P$_4$(SitBu$_3$)$_3$] (M = Li, Na) can be transformed into the unsaturated triphosphenides M[tBu$_3$SiPPPSitBu$_3$] and the monophosphanediide M$_2$[PSitBu$_3$].[5]

Otherwise, the reaction of P$_4$ with M[SitBu$_3$] (M = Li, Na, K) and Na[SiPhtBu$_2$] in a molar ratio of 1 : 2 produces the tetraphosphendiides M$_2$[tBu$_3$SiPP=PPSitBu$_3$] (M = Li, Na, K) (M$_2$[**1**]) and Na$_2$[tBu$_2$PhSiPP=PPSiPhtBu$_2$] which dimerize in weakly polar solvents to the octaphosphides M$_4$[P$_8$(SitBu$_3$)$_4$] (M = Li, Na, K) and Na$_4$[P$_8$(SitBu$_2$Ph)$_4$].[6–8] It is interesting to note that the potassium silanide K[SitBu$_3$] causes the decomposition of the tetraphosphendiide K$_2$[**1**]; K[tBu$_3$SiPPPSitBu$_3$] and K$_2$[PSitBu$_3$] are formed.[8] Contrary to the lithium tetraphosphide Li$_3$[P$_4$(SitBu$_3$)$_3$] (Li$_3$[**2**]), the related potassium tetraphosphide K$_3$[**2**] is as yet unknown.



Scheme 1 Syntheses of supersilylated phosphanides and phosphenides M$_2$[**1**], M$_3$[**2**], M[**3**], and M$_4$[P$_8$(SitBu$_3$)$_4$] (M = Li, Na, K). (I) THF, r.t. (II) + 1 M[SitBu$_3$] (M = Li, Na, K), benzene r.t. (III) −M$_2$[PSitBu$_3$] (M = Li, Na, K), THF r.t. (IV) hexane r.t.

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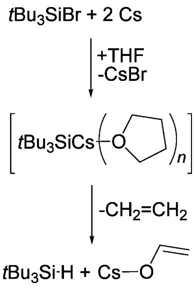
‡ The HTML version of this article has been enhanced with colour images.

The triphosphenide K[tBu$_3$SiPPPSitBu$_3$] (K[**3**]) may be produced *via* an intermediary tetraphosphide K$_3$[**2**].[8]

We have now discovered that the thermolysis reaction of Li[**3**], Na[**3**], K[**3**], and Cs[**3**] is rather similar to that of the analogous sodium triazenide Na[tBu$_3$SiNNNSitBu$_3$].[9–11] In this context we have found that the caesium triphosphenide Cs[**3**] is more stable than its homologues Li[3],[5] Na[3],[12] and K[3].[8] Therefore, Cs[3] represents an ideal compound to investigate the properties of the triphosphaallyl anion. In this paper the structural and chemical features of two novel caesium allyl compounds, the triphosphenide Cs[3] and the enolate Cs[OCH=CH$_2$], respectively, have been described.

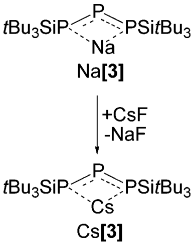
Results and discussion

The successful synthesis of K[**3**] from P$_4$ with 3 equivalents of K[SitBu$_3$] in tetrahydrofuran, raised the question whether the caesium triphosphenide Cs[**3**] can be prepared by an analogous synthetic route as that of K[**3**]. However, our efforts to synthesize the caesium silanide Cs[SitBu$_3$] as tetrahydrofuran complex failed. When tBu$_3$SiBr was treated with an excess of caesium metal in tetrahydrofuran at room temperature, the caesium enolate Cs[OCH=CH$_2$] and the supersilane tBu$_3$SiH formed rather than the silanide Cs[SitBu$_3$]. Single crystals of the caesium enolate Cs[OCH=CH$_2$], which is nearly insoluble in organic solvents, were obtained from the reaction solution (see Scheme 2).



Scheme 2 Formation of the caesium enolate Cs[OCH=CH$_2$].

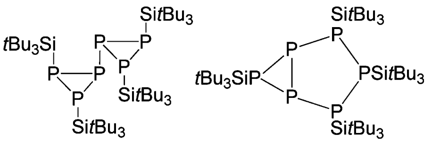
As shown in Scheme 3, the reaction of Na[**3**], which has been generated by P$_4$ degradation with 3 equivalents of Na[SitBu$_3$], and CsF conveniently produces Cs[**3**] in THF at ambient temperature.



Scheme 3 Synthesis of the caesium triphosphenide Cs[3].

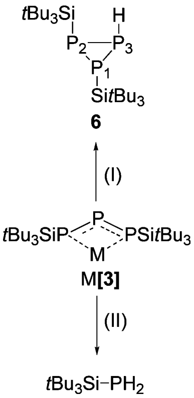
The triphosphenides Li[3], Na[**3**], K[**3**], and Cs[**3**] are sensitive to oxygen and moisture. Oxidation of the triphosphenides Li[**3**], Na[3], K[**3**], and Cs[**3**] with TCNE leads to the formation of the hexaphosphanes **4** and **5** (Fig. 1).[12]

The triphosphenide Cs[**3**] reacts spontaneously with acids, as the homologues Li[**3**], Na[**3**], and K[3] do (see Scheme 4).[12]



4 **5**

Fig. 1 1,1′-Bicyclotriphosphane **4** and bicyclo[3.1.0]hexaphosphane **5**.



Scheme 4 Protonation of the triphosphenides Li[**3**], Na[**3**], K[**3**], and Cs[**3**]. (I) + 1 CF$_3$CO$_2$H, THF r.t. (II) excess of CF$_3$CO$_2$H, THF r.t.

Treatment with a stoichometric amount of electrophile such as H$^+$ in CF$_3$CO$_2$H leads to the formation of the cyclotriphosphane derivative **6** exclusively. However, the reaction of Cs[**3**] with an excess of acids *e.g.* CF$_3$CO$_2$H produces the supersilylphosphane tBu$_3$SiPH$_2$ and phosphorus. *Ab initio* calculations reveal that neutral compounds with P$_3$ framework like HP$_3$(SiH$_3$)$_2$ prefer the cyclic form whereas in P$_3$(SiH$_3$)$_2^-$ the anionic acyclic allylic conjugation is more stable than the cyclic isomer.[12]

It is interesting to note that the triphosphenides Li[**3**], Na[**3**], and K[**3**] are labile compounds. We found that *in vacuo* Li[**3**], Na[**3**], and K[**3**] rapidly decompose at ambient temperature. Obviously the removal of THF ligands led to fragmentation of the triphosphaallyl anion in the case of Li[**3**], Na[**3**], and K[**3**], respectively, with the formation of the monophosphanides M[P(SitBu$_3$)$_2$] (M = Li, Na, K).[14] An analogous reaction could be observed in triazenide thermolysis. We found that the triazenides M[tBu$_3$SiNNNSiMetBu$_2$] (M = Li, Na) eliminate N$_2$ at room temperature whereas Na[tBu$_3$SiNNNSitBu$_3$] is more stable and decomposes at temperatures above 210 °C.[11]

In contrast to its homologues the caesium triphosphenide Cs[**3**] is stable *in vacuo*. However, Cs[**3**] decomposes in benzene slowly at room temperature. Thereby the ^{31}P NMR spectrum of the solution of Cs[**3**] thermolysis reveals several signals. Surprisingly, one of these signals can be assigned to the diphosphene tBu$_3$SiP=PSitBu$_3$.[13] The formation of tBu$_3$SiP=PSitBu$_3$ is yet unclear.[14]

Generally, the NMR spectra of caesium triphosphenide Cs[**3**] resemble those of the related lithium, sodium, and potassium triphosphenides Li[**3**], Na[**3**], and K[**3**].[5,8,12] The ^{31}P{^{1}H}NMR spectrum of the triphosphenide Cs[**3**] features two signals with the splitting pattern of an AX$_2$ spin system in the range for the unsaturated two-coordinate phosphorus atoms. The ^{31}P NMR data of triphosphenides Li[3], Na[3], K[**3**], and Cs[**3**] are listed in Table 1.

Table 1 ^{31}P NMR spectra of triphospenides M[tBu$_3$SiP$_X$P$_A$P$_X$SitBu$_3$] (M = Li, Na, K, Cs)

	Li[**3**][5]	Na[**3**][12]	K[**3**][8]	Cs[**3**]
$\delta(P_A)$	729.8^a	730.0^a	732.5^a	745.4^b
$\delta(P_X)$	226.6^a	212.5^a	230.0^a	236.2^b
$^1J_{PP}$	442.0 Hz^a	552.7 Hz^a	550.0 Hz^a	561.2 Hz^b

^{a} In d$_8$-THF. ^{b} In C$_6$D$_6$.

Single crystals of caesium enolate Cs[OCH=CH$_2$] suitable for X-ray crystallography were grown from a tetrahydrofuran solution of the reaction mixture at ambient temperature. The structure of the caesium enolate Cs[OCH=CH$_2$] is shown in Fig. 2 and 3. It is interesting to note that Cs[OCH=CH$_2$] represents the first structurally characterized binary metal enolate solely with hydrogen substituents on the C atoms. Surprisingly, the Cs atoms in Cs[OCH=CH$_2$] are coordinated by four enolate anions. Two of these enolate units coordinate in η^3-fashion while the other two anions are bound to the Cs cation *via* the lone pair of their enolate-O atom. Thereby, the O atoms of the enolate anions connect two infinite neighbouring chains composed of Cs cations and η^3-coordinated enolate anions, as shown in Fig. 2 and 3. The solid-state structure, therefore, features a three-dimensional network with enolate anions as bridging units, as depicted in Fig. 3. Obviously, this network results in the poor solubility of Cs[OCH=CH$_2$] in organic solvents.

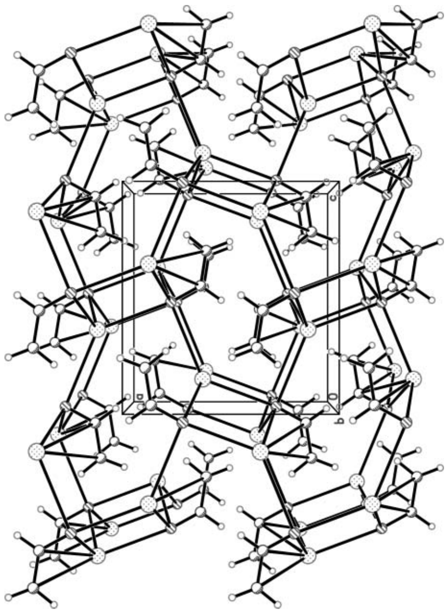


Fig. 2 Crystal packing diagram for Cs[OCH=CH$_2$].

Table 2 Bond lengths and bond angles of enolates M[OCH=CH$_2$]

M	C=C/Å	O–C/Å	O–C–C/°
Li(L)$_n$[15]	1.28(1)–1.40(1)	1.32(1)–1.45(1)	125.1(10)–128.9(9)
Cs	1.35(1)	1.29(1)	127.8(4)
Sr(L)$_n$[16]	1.42(1)	1.41(1)	114.3(4)
Ba(L)$_n$[16]	1.29(1)–1.35(1)	1.31(1)–1.33(1)	126.7(1)–129.1(1)
Sc(L)$_n$[17]	1.30(1)	1.34(1)	126.1(4)
Y(L)$_n$[18]	1.29(1)	1.32(1)	128.0(6)
Ti(L)$_n$[19]	1.31(1)	1.33(1)	128.4(4)
Nb(L)$_n$[20]	1.26(2)–1.33(4)	1.35(2)–1.42(3)	119.0(20)–126.0(20)
Ce(L)$_n$[21]	1.31(1)	1.33(1)	125.5(4)

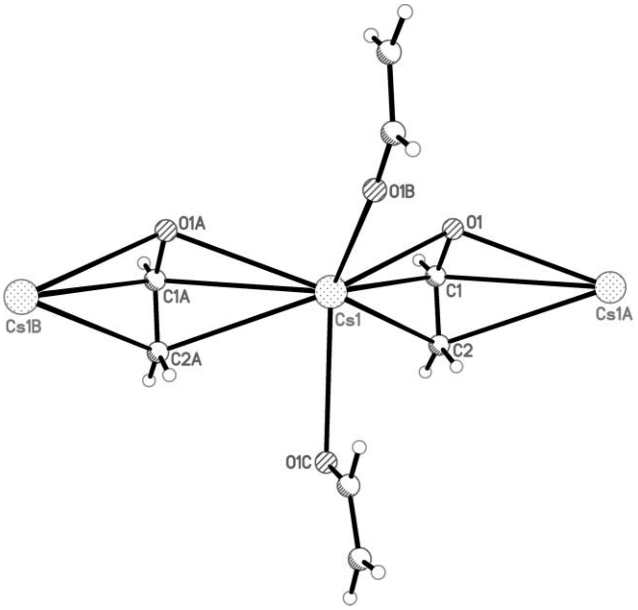


Fig. 3 Molecular structure of Cs[OCH=CH$_2$] in the solid state. Selected bond lengths [Å] and bond angles [°]: Cs(1)–O(1)#1 2.974(3), Cs(1)–O(1)#2 3.160(3), Cs(1)–O(1) 3.189(2), Cs(1)–C(1) 3.407(3), Cs(1)–C(2) 3.490(3), Cs(1)–C(1)#2 3.541(7), Cs(1)–C(2)#4 3.678(3), Cs(1)–C(2)#6 3.712(7), O(1)–C(1) 1.288(6), O(1)–Cs(1)#1 2.974(3), O(1)–Cs(1)#6 3.160(3), C(1)–C(2) 1.350(11), O(1)#1–Cs(1)–O(1)#2 133.00(9), O(1)#1–Cs(1)–O(1) 92.44(7), O(1)#2–Cs(1)–O(1) 108.57(4), O(1)–Cs(1)–O(1)#3 123.00(11), O(1)#1–Cs(1)–C(1)#3 114.45(9), O(1)–Cs(1)–C(1)#3 121.31(11), O(1)#2–Cs(1)–C(1) 90.17(12), C(1)#3–Cs(1)–C(1) 110.66(13), O(1)#2–Cs(1)–C(2)#3 68.09(11), O(1)–Cs(1)–C(2)#3 131.25(10), C(1)–Cs(1)–C(2)#3 113.40(9), O(1)#1–Cs(1)–C(2) 126.47(6), C(2)#3–Cs(1)–C(2) 106.82(12), O(1)#1–Cs(1)–C(1)#2 111.81(10), O(1)–Cs(1)–C(1)#2 115.18(6), C(1)–Cs(1)–C(1)#2 102.03(12), C(2)–Cs(1)–C(1)#2 79.64(12), C(1)–O(1)–Cs(1) 88.49(16), O(1)–C(1)–C(2) 127.8(5), O(1)–C(1)–Cs(1) 69.31(13), C(2)–C(1)–Cs(1) 82.2(2), C(1)–C(2)–Cs(1) 75.29(16). Symmetry transformations used to generate equivalent atoms: #1 $-x,-y+1,-z+1$; #2 $-x+1/2,-y+1,z-1/2$; #3 $x,y+1,z$; #4 $x-1/2,y,-z+1/2$; #5 $x-1/2,y+1,-z+1/2$ #6 $-x+1/2,-y+1,z+1/2$; #7 $x,y-1,z$; #8 $x+1/2,y,-z+1/2$; #9 $x+1/2,y-1,-z+1/2$.

The metrical parameters of the enolate moiety of Cs[OCH=CH$_2$] are compared with those of other metal enolates in Table 2. The enolate C–O distance of 1.29(1) Å is on the short end of the range of values found in *e.g.* [Li$_3$(THF)$_3${(NtBu)$_3$S}(OCH=CH$_2$)],[15] the doubly enolate-brigded Sr or Ba diphenylmethanide dimers,[16] [Sc{(2,6-di-iPr-CH$_3$C$_6$H$_3$)NCMeCHC(Me)N(2,6-di-iPr-CH$_3$C$_6$H$_3$)}{NH(2,6-di-iPrCH$_3$C$_6$H$_3$)}(OCH=CH$_2$)],[17] [Y(CH$_3$-C$_5$H$_4$)$_2$(OCH=CH$_2$)]$_2$,[18] [TiCp$_2$Ti(OCH=CH$_2$)$_2$],[19] [Nb{N(3,5-Me$_2$C$_5$H$_3$)N(Ad)}$_3$(OCH=CH$_2$)],[20] and [Ce(TMP)$_2$(OCH=CH$_2$)][21] (Ad = adamantyl, TMP = 2,2,6,6-tetrametylpiperidinyl). The C=C bond length of 1.35(1) Å is within the range of lengths observed in enolates listed in Table 2. The enolate O–C–C bond angle of 127.8(5)° is comparable with known angles.

The crystal structure of the triphosphenide Cs[**3**] is shown in Fig. 4 and 5; selected bond lengths and angles can be found

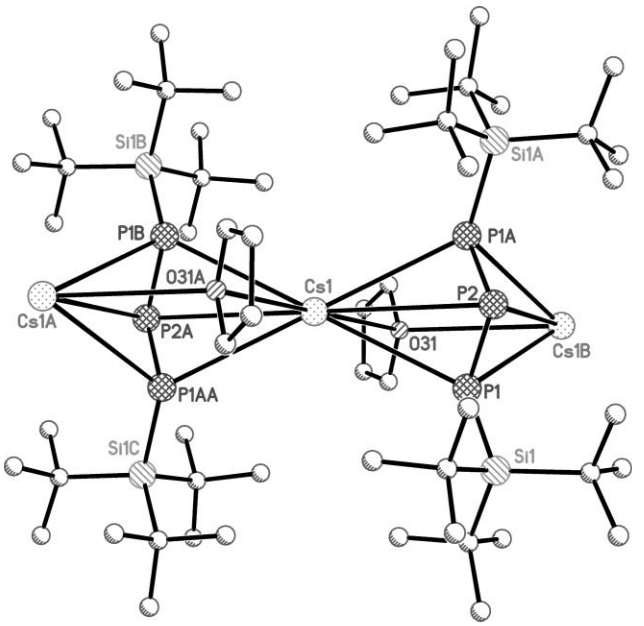


Fig. 4 Molecular structure of Cs[**3**] in the solid state. Hydrogen atoms omitted for clarity. Selected bond lengths [Å] and bond angles [°]: Cs(1)–P(1) 3.655(1), Cs(1)–O(31) 3.753(18), Cs(1)–P(2) 3.978(2), P(1)–P(2) 2.090(3), P(1)–Si(1) 2.271(3), P(2)–P(1)#3 2.090(3), Si(1)–C(2) 1.938(7), Si(1)–C(1) 1.948(9), O(31)–Cs(1)#4 3.753(18), P(1)#1–Cs(1)–P(1) 126.57(5), P(1)–Cs(1)–P(2)#2 148.58(3), P(1)–Cs(1)–P(2) 31.42(3), P(1)#3–P(2)–P(1) 103.67(16), P(1)–P(2)–Cs(1) 65.73(6). Symmetry transformations used to generate equivalent atoms: #1 $x,-y+1,-z+1$; #2 $-x,-y+1,-z+1$; #3 $-x,y,z$; #4 $-x,-y+1,z-1/2$; #5 $x,y,-z+1/2$.

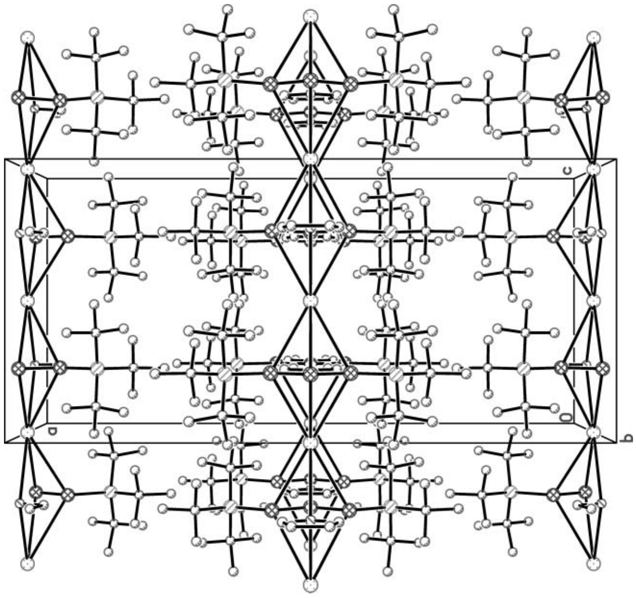


Fig. 5 Crystal packing diagram for Cs[**3**].

in the corresponding caption. X-Ray quality crystals of Cs[**3**] (orthorhombic, *Cmcm*) were grown from tetrahydrofuran. In contrast to the structures of monomeric Na[**3**] and dimeric K[**3**], the supersilylated triphosphenide Cs[**3**] features a polymer in the solid state as Cs[OCH=CH$_2$] does. Although the binding mode of both allyl anions, [*t*Bu$_3$SiPPPSi*t*Bu$_3$]$^-$ and [OCH=CH$_2$]$^-$, is quite similar, however, the solid-state structure of Cs[**3**] features an infinite chain of Cs cations and [*t*Bu$_3$SiPPPSi*t*Bu$_3$] anions. By contrast, a three-dimensional network of Cs cations and [OCH=CH$_2$] anions is observed in the structure of Cs[OCH=CH$_2$].

Table 3 Bond lengths [Å] and bond angles [°] of triphosphenides Na[**3**], K[**3**], and Cs[**3**]

	Na[**3**][12]	K[**3**][8]	Cs[**3**]
P–P	2.096(20) av	2.072(2)	2.090(3)
M–P	3.113(20) av	3.476(2) av	3.766(2) av
Si–P	2.303(20) av	2.270(1) av	2.271(3) av
Si–C	1.948(20) av	1.952(5) av	1.941(9) av
P–P–P	104.2(11) av	101.1(1)	103.7(2)

The molecular structure of the triphosphenide Cs[**3**] shows two short PP bonds and an almost planar W-shaped SiPPPSi skeleton with a P–P distance of 2.090(3) Å. This distance is in the range of PP double bonds, comparable with those found in the structures of Na[**3**] and K[**3**] (Table 3). As depicted in Fig. 4, the silyl-substituted triphosphaallylic anions are bridged by Cs cations to form a polymer in solid state. Therefore each of the triphosphenide anions in Cs[**3**] features six P–Cs contacts (P–Cs distance: 3.766(2) Å, average) for every Cs atom. However, these contacts are longer than the P–Cs bonds in Cs[PHSi*t*Bu$_3$] and in other structural characterized monophosphanides.[22] Apart from these P atoms, the Cs atoms are coordinated by two tetrahydrofuran molecules.

It is interesting to note that both caesium allyl compounds, Cs[OCH=CH$_2$] and Cs[**3**], have a solid-state structure in which the Cs cation has the coordination number eight. However, due to steric repulsion of the supersilyl groups the solid-state structure of the triphosphenide Cs[**3**] features an alternated arrangement of the triphosphaallylic anions, whereas in contrast to that the enolate anions of Cs[OCH=CH$_2$] are arranged in a congruent fashion.

Experimental

General procedures

All experiments were carried out under dry argon with strict exclusion of air and moisture using standard Schlenk techniques or a glove box. *t*Bu$_3$SiBr,[23,24] Na[Si*t*Bu$_3$],[23,24] and Na[**3**][5] were prepared according to literature procedures. The solvents (benzene, toluene, tetrahydrofuran) were distilled from sodium/benzophenone prior to use.

The triphosphenide Cs[**3**] is extremely moisture and oxygen sensitive. Therefore, the analysis is limited to NMR, UV and X-ray structure determination. The NMR spectra were recorded on a Bruker AM 250, a Bruker DPX 250, a Bruker Avance 300 and a Bruker Avance 400 spectrometer. The ^{29}Si NMR spectra were recorded using the INEPT pulse sequence with empirically optimised parameters for polarisation transfer from the *t*Bu substituents. Abbreviations: s = singlet; d = doublet; t = triplet; q = quartet; mult = multiplet; br = broad; m = meta; o = ortho; p = para.

Reaction of Cs with *t*Bu$_3$SiBr

Cs metal (0.60 g, 4.5 mmol) was added to a solution of *t*Bu$_3$SiBr (0.20 g, 0.71 mmol) in THF (5 cm^3). The reaction mixture was stirred for 2 h at ambient temperature. According to the ^{1}H, ^{13}C and the ^{29}Si NMR data the supersilane *t*Bu$_3$SiH was formed as a soluble main product. X-Ray quality crystals of Cs[OCH=CH$_2$] were grown from the reaction mixture at 2 °C. Yield: 0.1 g (80%). *t*Bu$_3$SiH: δ_H (250 MHz; C$_6$D$_6$; Me$_4$Si) 1.11 (27 H, s, *t*Bu), 3.54 (1 H, s, SiH). $\delta_C\{^1H\}$ (75.45 MHz; C$_6$D$_6$; Me$_4$Si) 21.0 (*C*Me$_3$), 30.8 (C*Me*$_3$). $\delta_{Si}\{^1H\}$ (79.49 MHz; C$_6$D$_6$; Me$_4$Si) 17.7 (Si*t*Bu$_3$). Cs[OCH=CH$_2$]: Found: C, 14.3; H, 2.2. C$_2$H$_3$CsO requires C, 13.6; H, 1.7.

Reaction of Na[3] with CsF

CsF (0.16 g, 1.1 mmol) in tetrahydrofuran (10 cm^3) was added to 6.3 cm^3 of a 0.2 M solution of Na[**3**] (1.3 mmol) in THF at ambient temperature and stirred for 2 days. According to the ^{31}P NMR spectrum the triphosphenide Cs[**3**] was formed quantitatively. X-Ray quality crystals of Cs[**3**] were obtained after the reaction mixture had been concentrated *in vacuo* to a volume of 5 cm^3 and kept at ambient temperature for 1 month. Yield: 0.55 g (72%). Selected data for Cs[P$_3$(Si*t*Bu$_3$)$_2$]·THF, Cs[**3**]·THF: δ_H (250 MHz; C$_6$D$_6$; Me$_4$Si) 1.49 (54 H, br, *t*Bu), 1.42 (2 H, m, THF-CH$_2$), 3.53 (2 H, m, THF-OCH$_2$). $\delta_C\{^1H\}$ (75.45 MHz; C$_6$D$_6$; Me$_4$Si) 25.3 (THF-*C*H$_2$), 25.5 (br, *C*Me$_3$), 32.8 (C*Me*$_3$), 68.9 (THF-O*C*H$_2$). $\delta_P\{^1H\}$ (162.03 MHz, C$_6$D$_6$; H$_3$PO$_4$) see Table 1. $\delta_{Si}\{^1H\}$ (79.49 MHz; C$_6$D$_6$; Me$_4$Si) 18.9 (td, $^1J_{SiP} + {}^3J_{SiP}$ 64.1, $^2J_{SiP}$ 10.0, Si*t*Bu$_3$). UV/vis: λ_{max}(benzene)/nm 499 (ε/dm^3 mol^{-1} cm^{-1} 14) and 551 (11).

Reaction of Cs[3] with CF$_3$CO$_2$H

CF$_3$CO$_2$H (0.25 cm^3, 3.4 mmol) was added to a solution of Cs[**3**] (0.2 mmol) in 1 cm^3 THF at ambient temperature and stirred for 3 h. According to the ^{31}P NMR spectrum the phosphane *t*Bu$_3$SiPH$_2$[25] was formed nearly quantitatively. CF$_3$CO$_2$H (0.02 cm^3, 0.2 mmol) was added to a solution of Cs[**3**] (0.2 mmol) in 1 cm^3 THF at ambient temperature and stirred for 3 h. According to the ^{31}P NMR spectrum the cyclotriphosphane **6** was formed as the main product (60% P). **6**: δ_H (250 MHz; C$_6$D$_6$; Me$_4$Si) 1.30 (54 H, m, *t*Bu). δ_P (162.03 MHz; C$_6$D$_6$; H$_3$PO$_4$, P numbering see Scheme 4)[26] −247.5 (1 P, m, $^1J_{P(1)P(2)}$ −187.1, $^1J_{P(1)P(3)}$ −142.3, $^2J_{P(1)H}$ 17.1, P(1)Si*t*Bu$_3$), −260.1 (1 P, m, $^1J_{P(1)P(3)}$ −187.1, $^1J_{P(2)P(3)}$ −223.4, $^2J_{P(2)H}$ 6.3, P(2)Si*t*Bu$_3$)), −260.7 (1 P, m, $^1J_{P(1)P(2)}$ −187.1, $^1J_{P(2)P(3)}$ −223.4, $^1J_{P(3)H}$ 138.0, P(3)H). (lit.,[12] −246.9 (1 P, m, $^1J_{P(1)P(2)}$ −188.0, $^1J_{P(1)P(3)}$ −141.3, $^2J_{P(1)H}$ 16.6, P(1)Si*t*Bu$_3$), −259.5 (1 P, m, $^1J_{P(1)P(2)}$ −188.0 $^1J_{P(2)P(3)}$ −224.2, $^2J_{P(2)H}$ 6.9, P(2)Si*t*Bu$_3$), −260.1 (1 P, m, $^1J_{P(1)P(3)}$ −141.3, $^1J_{P(2)P(3)}$ −224.2, $^1J_{P(3)H}$ 137.1, P(3)H)). $\delta_{Si}\{^1H\}$ (79.49 MHz; C$_6$D$_6$; Me$_4$Si) 27.4 (m, Si*t*Bu$_3$). *t*Bu$_3$SiPH$_2$: δ_H (250 MHz; C$_6$D$_6$; Me$_4$Si) 1.09 (27 H, d, $^4J_{PH}$ 0.49, *t*Bu), 0.94 (1 H, d, $^1J_{PH}$ 186, HP). $\delta_C\{^1H\}$ (75.45 MHz; C$_6$D$_6$; Me$_4$Si) 23.1 (d, $^2J_{PC}$ 5.9, *C*Me$_3$), 30.7 (d, $^3J_{PC}$ 2.4, C*Me*$_3$). δ_P (162.03 MHz; C$_6$D$_6$; H$_3$PO$_4$) −264.4 (t, $^1J_{PH}$ 186). $\delta_{Si}\{^1H\}$ (79.49 MHz; C$_6$D$_6$, Me$_4$Si) 24.1 (d, $^1J_{SiP}$ 33.2, Si*t*Bu$_3$).

Crystal structure determinations of Cs[OCH=CH$_2$] and Cs[3]

Data collections for Cs[**3**] and Cs[OCH=CH$_2$] were performed on a STOE IPDS-II two-circle diffractometer with graphite-monochromated Mo-Kα-radiation (λ = 0.71073 Å). The structures were solved with direct methods[27] and refined against F^2 by full-matrix least-squares calculations[28] (Table 4). Absorption corrections were performed with the MULABS[29] option in PLATON.[30] All non-H atoms have been refined anisotropically, whereas the H atoms have been treated with a riding model.

CCDC reference numbers 648996 (Cs[OCH=CH$_2$]), 648997 (Cs[**3**]).

For crystallographic data in CIF or other electronic format see DOI: 10.1039/b714339g

Conclusions

In contrast to the preparation of tetrahydrofuran-solvated silanides M[Si*t*Bu$_3$] (M = Li, Na, K), our efforts to synthesize the caesium silanide Cs[Si*t*Bu$_3$] as the tetrahydrofuran complex failed. When *t*Bu$_3$SiBr was treated with an excess of caesium

Table 4 Crystal data and experimental details for Cs[OCH=CH$_2$] and Cs[**3**]

	Cs[OCH=CH$_2$]	Cs[**3**]
Empirical formula	C$_2$H$_3$CsO	C$_{28}$H$_{62}$CsOP$_3$Si$_2$
Formula weight	175.95	696.78
Temperature/K	173(2)	173(2)
Crystal size/mm^3	0.28 × 0.25 × 0.11	0.34 × 0.27 × 0.26
Crystal system	Orthorhombic	Orthorhombic
Space group	*Pnma*	*Cmcm*
a/Å	7.9917(11)	25.516(2)
b/Å	5.6041(9)	12.8382(11)
c/Å	8.5828(13)	11.8824(10)
V/Å^3	384.39(10)	3892.4(6)
Z	4	4
calcd. density/Mg m^{-3}	3.040	1.189
μ/mm^{-1}	9.404	1.153
Index ranges	$-10 \le h \le 10, -7 \le k \le 7, -11 \le l \le 10$	$-30 \le h \le 26, -13 \le k \le 15, -14 \le l \le 14$
θ-range/°	4.34 to 27.59	3.55 to 25.37
No. of reflns. collected	4426	9944
No. of indep. reflns.	491	1899
R_{int}	0.0647	0.0293
Goodness-of-fit (F^2)	1.183	1.074
$R1$, $wR2$ [$I > 2\sigma(I)$]	$R1 = 0.0250$, $wR2 = 0.0637$	$R1 = 0.0941$, $wR2 = 0.2203$
$R1$, $wR2$ indices (all data)	$R1 = 0.0253$, $wR2 = 0.0639$	$R1 = 0.0974$, $wR2 = 0.2228$
Largest diff. peak and hole/e Å^{-3}	1.079 and −1.343	2.054 and −2.869

metal in tetrahydrofuran at room temperature, the caesium enolate Cs[OCH=CH$_2$] and the supersilane tBu$_3$SiH formed as main products, rather than the silanide Cs[SitBu$_3$]. Actually, the triphosphenide Cs[**3**] was accessible from the reaction of CsF with the sodium triphosphenide Na[**3**] at room temperature in tetrahydrofuran. In contrast to the structures of homologue triphosphenides Na[**3**] and K[**3**] which possess a monomeric (Na[**3**]) or dimeric (K[**3**]) structure, the triphosphenide Cs[**3**] features a polymer in the solid state (orthorhombic, *Cmcm*). X-Ray quality crystals of the enolate Cs[OCH=CH$_2$] (orthorhombic, *Pnma*) were obtained from tetrahydrofuran at ambient temperature. It is interesting to note that both caesium allyl compounds, Cs[OCH=CH$_2$] and Cs[**3**], have a solid state structure in which the Cs cation is coordinated in η^3-fashion from two allylic anions. However, due to steric repulsion of the supersilyl groups in Cs[**3**] the solid-state structure of the triphosphenide Cs[**3**] features an alternate arrangement of the triphosphaallylic anions, whereas the enolate anions of Cs[OCH=CH$_2$] are arranged in a congruent fashion. Moreover, the solid state structure of Cs[OCH=CH$_2$] features a three-dimensional network with enolate anions as bridging units. Obviously, this network results in the poor solubility of Cs[OCH=CH$_2$] in organic solvents.

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