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About the Reaction of $BeCl_2$ with the Carbodiphosphorane Addition Compound $O_2C{\leftarrow}C(PPh_3)_2$ and its Hydrolysis Product $Ph_3PCHP(O)Ph_2$

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In Memory of Professor Kurt Dehnicke

Keywords: Beryllium; X-ray diffraction; Ylides; Carbodiphosphorane adducts; $(BeO)_5$ ring

Abstract. Reaction of $BeCl_2$ and $(PPh_4)[Be_2Cl_6]$ with $Ph_3PCHP(O)Ph_2$ (**2**) and of $BeCl_2$ with $O_2C{\leftarrow}C(PPh_3)_2$ (**3**) were studied under various conditions. Whereas the addition compound of **2** with $BeCl_2$ could only traced by ^{31}P NMR spectroscopy the molecular structure of the O-addition compound $[Ph_3PCH_2P(OBeCl_3)Ph_2]{\cdot}0.75CH_2Cl_2$ (**5**) from **2** and $(PPh_4)[Be_2Cl_6]$ could be performed. From **3** and $BeCl_2$ in dichloromethane crystals of $(H_2C\{PPh_3\}_2)[BeCl_4]$ (**6**) and $(H_2C\{PPh_3\}_2)Cl_2{\cdot}CH_2Cl_2$ (**7**) separated. The cluster $[Be_6(OH)_6Cl_5(O_2C_2\{PPh_3\}_2)_3]Cl$ (**8**) formed upon unintentionally admitting some humidity to the initial reaction mixture. In **8** each of the bidentate ligands **3** bridges two different beryllium atoms via the oxygen atoms. All compounds are characterized by X-ray diffraction analyses.

1 Introduction

The double ylide hexaphenylcarbodiphosphorane $C(PPh_3)_2$ (**1**)[1] has a bent conformation[2] and can be considered as a divalent carbon(0) atom, which is stabilized by two neutral phosphine ligands, thus attaining eight electrons. **1** is endowed with two high lying occupied MO's at the carbon atom of σ and π symmetry (HOMO and HOMO-1) which is established by NBO analysis. Those compounds are also named carbones[3] and were subjects of preparative[4] and theoretical studies.[5]

1 reacts easily with wet air to produce quantitatively the hydrolysis product $Ph_3PCHP(O)Ph_2$ (**2**)[1] and with CO_2 the addition compound $O_2CC(PPh_3)_2$ (**3**) is quantitatively formed as depicted in Equation (1) and Equation (2), respectively.[6] Similar addition compounds with CS_2 or COS also exist.

$$\mathbf{1} + H_2O \rightarrow Ph_3PCHP(O)Ph_2\ (\mathbf{2}) + C_6H_6 \qquad (1)$$

$$\mathbf{1} + CO_2 \rightarrow O_2CC(PPh_3)_2\ (\mathbf{3}) \qquad (2)$$

2 is also found in small amounts as byproduct during the preparation of **1**. As shown in Scheme 1 the compounds **2** and **3** have in common, that they are Lewis bases according to free pairs of electrons at carbon (**2**) or at oxygen atoms (**2** and **3**) prone to coordinate at various Lewis acids.

2 **3**

Scheme 1. Structures of the Lewis bases $Ph_3PCHP(O)Ph_2$ (**2**) and $O_2C{\leftarrow}C(PPh_3)_2$ (**3**).

The hydrolysis product **2** has also ylidic character and can be considered as derived from the ylide $Ph_3P = CH_2$ in which one proton is replaced by the $P(O)Ph_2$ group. However, the chemistry of **2** is only sparingly explored so far. Coordination of Lewis acids at the carbon atom and the oxygen atom is possible and the first compounds reported were $[Ph_3PCHP(OW\{CO\}_5)Ph_2]$[7] and the salt $[Ph_3PCH_2P(OAlBr_3)Ph_2][AlBr_4]$;[8] further neutral or cationic addition compounds of **2** were reported recently by us.[9]

Compound **2** is expected to coordinate at a Lewis acids according to coordination mode **I** to **IV** as depicted in Scheme 2. Main group or transition metal electron deficient species prefer **I** but also **III** is realized, however with **M** = H^+ at the carbon atom.[7] Cationic compounds of mode **II** exist with **M** = H^+ or Me^+;[10] no example with mode **IV** is known so far.

Since the first description 50 years ago the carbon dioxide adduct **3** has found no further attention until recently. **3** is insoluble in toluene and is unstable in halogenated hydrocarbons, where slow proton abstraction with formation of the cation $(HC\{PPh_3\}_2)^+$ could be traced by ^{31}P NMR spectroscopy. Scheme 3 shows the simplest and most reliable coordination modes of **3** with coordination to one or two Lewis acids. **3** can coordinate to a metal fragment via one oxygen atom[11] or can act as a chelating ligand[12] due to coordination modes **A** and

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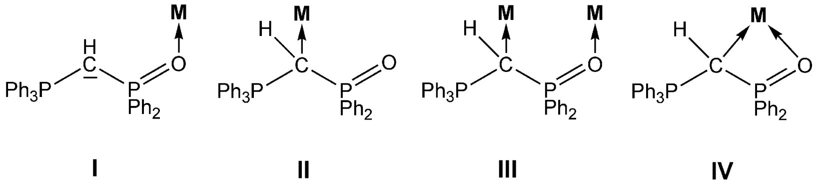
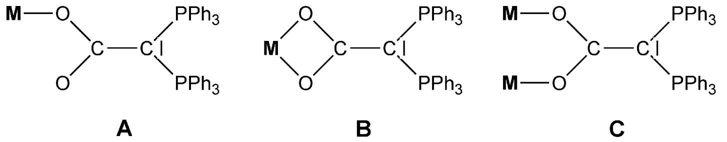


Scheme 2. Possible coordination modes **I** to **IV** of **2**.



Scheme 3. Possible coordination modes **A** to **C** of **3**.

B, respectively; complexes of **3** were also obtained as byproducts upon reactions of **1** with transition metal carbonyl complexes via a Wittig type reaction where both oxygen atoms stem from CO.[13] Compounds with mode **C** are not described so far.

Having in mind these properties we studied reactions of the Lewis bases **2** and **3** with $BeCl_2$ and of **2** with $[Be_2Cl_6]^{2-}$. The Be^{2+} cation is extremely small (ion radius of 27 pm), strongly polarizing and as a hard Lewis acid has a strong oxophilic character; the preferred coordination number is four but coordination number three is also found. Surprisingly, the number of crystal data of beryllium compounds is limited. Here we report on the results of the reaction of $BeCl_2$ with the ylide **2** and the CO_2 adduct **3**.

2 Results and Discussion

2.1 Reaction of 2 with $BeCl_2$ and $(PPh_4)[Be_2Cl_6]$

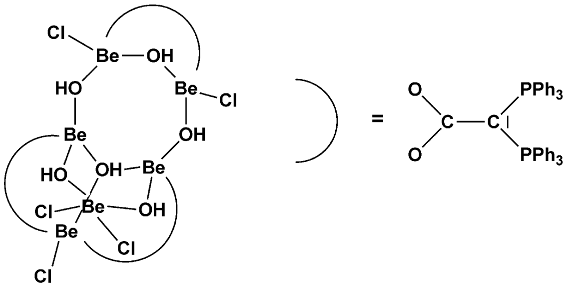
The reaction of $BeCl_2$ with **2** was performed in CH_2Cl_2 solution. In the ^{31}P NMR spectrum of the solution the two doublets of **2** at $\delta = 27.3$ and 20.6 ppm ($^2J(P,P) = 19.7$ Hz) have disappeared in favor of two new doublets at $\delta = 37.4$ and 18.5 ppm ($^2J(P,P) = 21.5$ Hz) indicative for adduct formation $Cl_2Be{\leftarrow}$**2** (**4**). For electronic reasons **4** must be dimeric or **2** is acting as a chelating ligand by additional HC–Be coordination. Layering of the DCM solution with *n*-pentane generated only thin fibrous crystals which were not suitable for X-ray analysis. Precipitation with *n*-pentane gave a colorless microcrystalline solid which is soluble in DMSO. In this solvent, however, a dramatic change in the shifts in the ^{31}P NMR spectrum has occurred with formation of two new doublets at $\delta = 23.6$ and 22.1 ppm ($^2J(P,P) = 14.1$ Hz). From other experiments we know that this signal is due to the cation $[Ph_3PCH_2P(O)Ph_2]^+$ $(H{\leftarrow}\mathbf{2})^+$. The same set of signals was found if pyridine was added to the DCM solution of **4**; crystals from these solution turned out to be $(H{\leftarrow}\mathbf{2})Cl$.

In a further run **2** was allowed to react with $(PPh_4)[Be_2Cl_6]$ in DCM. The $[Be_2Cl_6]^{2-}$ anion consists of two edge bridged tetrahedron where the chlorine bridges can easily be cleaved even by weak Lewis bases with ring opening.[14] Addition of equimolar amounts of **2** gives a clear solution. In the ^{31}P NMR spectrum of the reaction mixture two sets of doublets in 1:4 ratios were recorded indicating the formation of two different products. The minor product shows signals at $\delta = 36.1$ and 19.7 ppm with $^2J(P,P) = 17.9$ Hz and the signals of the major product appear at $\delta = 31.4$ and 19.7 ppm with $^2J(P,P) = 21.5$ Hz. No coupling between ^9Be (100 %, $I = 3/2$) and phosphorus could be measured; $^2J(Be,P)$ is probably too small to be detected. Layering of the solution with *n*-pentane gave an oil from which colorless crystals separated after several weeks. The crystals turned out to be the neutral product $[Ph_3PCH_2P(OBeCl_3)Ph_2]{\cdot}0.75CH_2Cl_2$ (**5**). Initially, we expected the formation of the salt $(PPh_4)[Ph_3PCHP(OBeCl_3)Ph_2]$ and the origin of the proton is as yet unclear; deprotonation of the solvent seems to be reliable. The IR spectrum exhibits two strong bands in the region of PO bond vibration at 1164 and 1113 cm^{-1}; related bands at 1184 and 1117 cm^{-1} were found in the spectrum of the cation $[Ph_3PCH_2P(O)Ph_2]^+$. To the best of our knowledge, **5** is the first compound with an all terminal Cl_3BeO unit. Only $Be_2Cl_5(\mu\text{-}OR)$ units were described so far, in which O*R* groups act as a bridging ligands.[15]

2.2 Reaction of $BeCl_2$ with 3

The reaction of $BeCl_2$ with the carbon dioxide adduct **3** was studied in several runs. A 1:1 ratio of the components in CH_2Cl_2 produced a clear solution from which after evaporation of the solvent an oily residue remained. The IR spectrum of the oil exhibits bands at 1547 and 1380 which can be assigned to the CO_2 group and were also found in the spectrum of the tin complex $[Cl_2Sn(OC(O)C(PPh_3)_2)]$.[11] No crystals separated from the oil even after storage of the oil for two months at low temperature. The ^{31}P NMR spectrum of the oil in CH_2Cl_2 exhibits five signals in a narrow range between $\delta =$ 21.7 and 20.1 ppm; the main signal is at $\delta = 21.5$ ppm. Layering the solution with *n*-pentane gave colorless crystals of $(H_2C\{PPh_3\}_2)[BeCl_4]$ (**6**) as the major product; further addition of *n*-pentane gave an oil from which crystals of $(H_2C\{PPh_3\}_2)Cl_2{\cdot}CH_2Cl_2$ (**7**) separated after some weeks. **6** and **7** are the result of loss of CO_2 of **3** followed by deprotonation of DCM. The cation in **6** exhibits a signal at $\delta = 19.2$ ppm in the ^{31}P NMR spectrum in $CDCl_3$ and the addition of (H←**1**) I to the solution gave rise to a new signal at $\delta = 20.0$ ppm for $(H\leftarrow\mathbf{1})^+$. The presence of the $BeCl_4$ anion prevents the cation from dissociation. The salt **6** is the first one belonging to the AB type; the other known salts with the same cation are of the AB_2 type.,[16,17]

In a second run the DCM solution of the oil was again layered with *n*-pentane. An oily precipitated from which after standing for several months two sorts of colorless crystals have grown. The minor product turned out to be the salt **7**. The major amount of crystals were found to be the unusual cluster compound $[Be_6(OH)_6Cl_5(O_2C_2\{PPh_3\}_2)_3]Cl$ (**8**). The formation of **8** needs contact to some humidity which probably was introduced by a leaking stopcock. The spine of **8** is a ten-membered ring of five Be^{2+} and five $OH^–$ ions and one exocyclic Be^{2+} ion (Scheme 4). The charge of the ring system is 11^+ (6 Be = 11^+, 6 OH = $6^–$, 5 Cl = $5^–$) and one of the six $OH^–$ groups acts as bridge between two beryllium atoms across the ring as shown in Scheme 2; one $Cl^–$ ion is free in the crystal lattice. Three molecules of **3** hold the assembly together as shown in Scheme 2.



Scheme 4. Simplified view of the cation of $[Be_6(OH)_6Cl_5(O_2C_2\{PPh_3\}_2)_3]Cl$ (**8**).

3 Crystal Structures

Crystallographic data could be obtained for the compounds **5**, **6**, **7**, and **8**; crystals were formed as described above and the molecular structures are shown in Figure 1, Figure 2, Figure 3, Figure 4, and Figure 5; crystallographic data are collected in Table 1; bond lengths and angles are summarized in Table 2, Table 3, Table 4, and Table 5.

3.1 Crystal Structure of $[Ph_3PCH_2P(OBeCl_3)Ph_2]\cdot0.75CH_2Cl_2$ (5)

The unit cell of **5** contains two independent molecules from which one is depicted in Figure 1. Related cationic compounds with the group 13 Lewis acids BF_3, BI_3 and $AlBr_3$ were described recently.[8,9] The P–O bond length in **5** amounts to 1.498(3) Å which is significantly shorter than the related average bond length in the cationic compounds (1.533(2) Å) and only slightly longer than in **2** (1.489(2) Å), which means that the PO π bonding is not very unbalanced by the coordination of the $BeCl_3$ group. A remarkable long Be–O bond length of 1.657(7) Å is found relative to the mean bond lengths in the DMSO complex $[Be(DMSO)_4]Cl_2$ (1.619 (5) Å)[18] and especially to those with a comparable Ph_3PO complex as in $[(NO_3)_2Be(OPPh_3)_2]$ were a mean value of 1.590 Å was recorded.[19] The Be–Cl bond lengths are in the range of those reported for tetrachloroberyllates but are slightly longer than in $BeCl_3$ adducts with N-donors.[15] The C–P bonds to C(1) differ by about 0.04 Å and correspond to single bonds; the different P–C bond lengths in **2**, amounting to 1.717(3) Å (PO) and 1.688(3) Å (PPh_3), have both increased to 1.841(5) Å and 1.803(5) Å, respectively, upon H^+ and $BeCl_3^–$ addition, directed to P–C single bonds. The most drastic change of about 1.2 Å has occurred due to loss of the π-type electron pair, which in **2** is involved in back bonding into PC_{Ph} σ* orbitals with formation of a partial double bond. According to rehy-

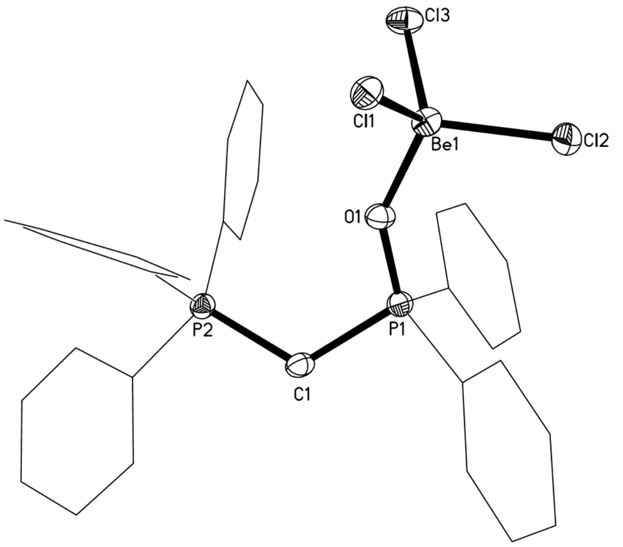


Figure 1. Molecular structure of $[Ph_3PCH_2P(OBeCl_3)Ph_2]\cdot0.75CH_2Cl_2$ (**5**) showing the atom numbering scheme The ellipsoids are drawn at a 40 % probability level; solvent molecule and hydrogen atoms are omitted for clarity.

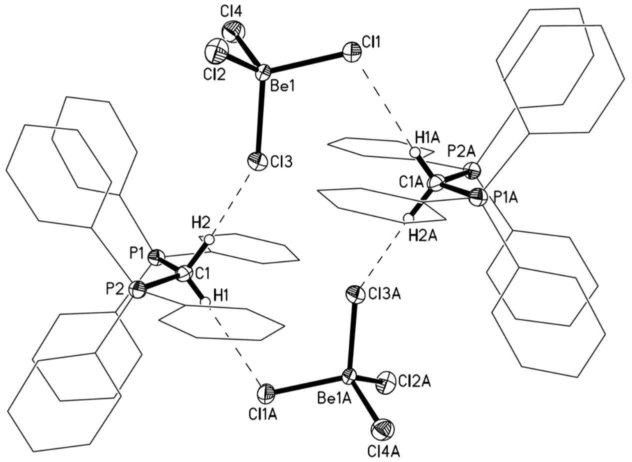


Figure 2. Molecular structure of $(H_2C\{PPh_3\}_2)[BeCl_4]\cdot CH_2Cl_2$ (**6**) showing the atom numbering scheme The ellipsoids are drawn at a 40 % probability level. Solvent molecule and hydrogen atoms are omitted for clarity. Compound **6** forms centrosymmetrical dimers via hydrogen bonding.

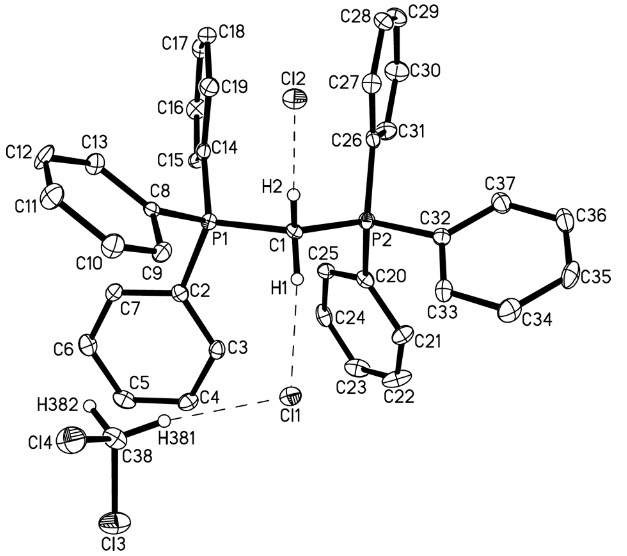


Figure 3. Molecular structure of $(H_2C\{PPh_3\}_2)Cl_2\cdot CH_2Cl_2$ (**7**) showing the atom numbering scheme The ellipsoids are drawn at a 40% probability level. The hydrogen atoms at the phenyl rings are omitted for clarity.

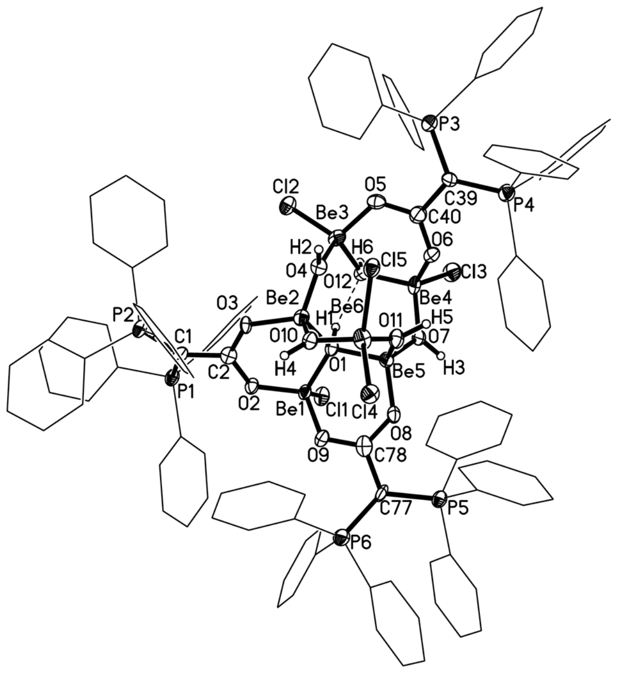


Figure 4. Molecular structure of the cation of $[Be_6(OH)_6Cl_5(O_2C_2\{PPh_3\}_2)_3]Cl\cdot 3.25CH_2Cl_2$ (**8**) showing the atom numbering scheme The ellipsoids are drawn at a 40% probability level; solvent molecules and the hydrogen atoms are omitted for clarity.

bridization at C(1) the P(1)–C(1)–P(2) angle has decreased from 117.5(2)° in **2** to 118.6(3)° in **5**. A very acute P(1)–O(1)–Be(1) angle of 143.9(3) is measured and contrasts to those found in $[(NO_3)_2Be(OPPh_3)_2]$ being at 173 and 159°.[23]

3.2 Crystal Structure of $(H_2C\{PPh_3\}_2)[BeCl_4]\cdot CH_2Cl_2$ (6)

As shown in Figure 2 two $(H_2C\{PPh_3\}_2)[BeCl_4]$ units form a centrosymmetric dimer and anions and cations are connected by four hydrogen bridges. The Be–Cl bonds involved in bridging are slightly longer than the free ones. The Cl–Be–Cl angles range between 108.9(3)° and 113.1(2)°; the deviation from the ideal tetrahedral angle is larger than in related salts.[20] The DCM molecules are incorporated into the holes between the dimers. No deviation of the parameters of the cation relative to those of the related chlorides **7**·DME and **7**·CH_2Cl_2 could be recognized.

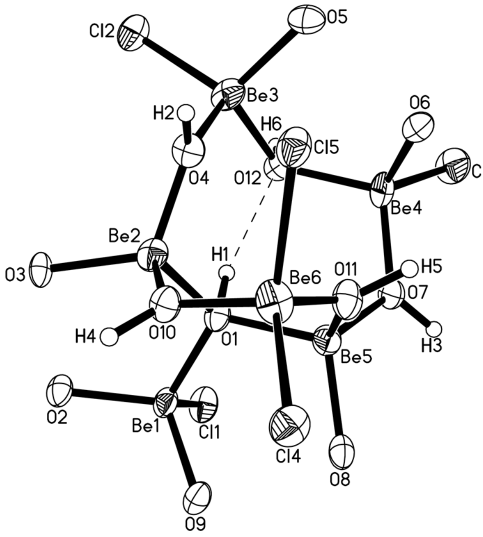


Figure 5. Environment of the Be_6 core of $[Be_6(OH)_6Cl_5(O_2C_2\{PPh_3\}_2)_3]^+$ (**8**); each pair O(2/3), O(5/6), and O(8/9) belong to one ligand of **3**.

3.3 Crystal Structures of $(H_2C\{PPh_3\}_2)Cl_2\cdot CH_2Cl_2$ (7)

The bond lengths of the phosphorus atoms to the sp^3 hybridized atom C(1) are due to a normal single bond averaging to 180.7(3) pm and are slightly shorter than those in **6** (181.7(4) pm). The bonds are longer than to the sp^2 hybridized phenyl carbon atoms (average 179.4 pm). The molecular structure of **7** is closely related to that of $(H_2C\{PPh_3\}_2)Cl_2\cdot$DME published earlier.[21] In all compound with the dication the P(1)–C(1)–P(1) angles are close together ranging between 111 and 113°. The different solvents included in the crystal do not markedly influence the bonding parameters of the dication $(H_2C\{PPh_3\}_2)^+$. In the related salt $(H_2C\{PPh_3\}_2)Cl_2\cdot$DME the DME molecule is disordered and not connected by hydrogen bridges, whereas the DCM molecule in **7** forms bridges to the chloride anions as depicted in Figure 3. In both compounds contacts are formed between H(1) to Cl(1) and H(2) to Cl(2) with C(1)···Cl(1)/C(1)···Cl(2) distances of 336.3(3)/332.4(3) in $(H_2C\{PPh_3\}_2)Cl_2\cdot$DME and 338.2(3)/337.8(3) in **7**.

3.4 Crystal Structure of $[Be_6(OH)_6Cl_5(O_2C_2\{PPh_3\}_2)_3]Cl\cdot 3.25CH_2Cl_2$ (8)

The molecular structure of the $[Be_6(OH)_6Cl_5(O_2C_2\{PPh_3\}_2)_3]^+$ cation is shown in Figure 4: Figure 5 depicts the environments of the six Be^{2+} cations. The beryllium atom and the OH groups form a 10-membered ring bridged by the O(1)H(1) group. A

Table 1. Crystallographic data of the compounds $[Ph_3PCH_2P(OBeCl_3)Ph_2]{\cdot}0.75CH_2Cl_2$ (**5**), $(H_2C\{PPh_3\}_2)[BeCl_4]{\cdot}CH_2Cl_2$ (**6**), $(H_2C\{PPh_3\}_2)Cl_2{\cdot}CH_2Cl_2$ (**7**), and $[Be_6(OH)_6Cl_5(O_2C_2\{PPh_3\}_2)_3]Cl{\cdot}3.25CH_2Cl_2$ (**8**).

	5	**6**	**7**	**8**
formula	$C_{31.75}H_{28.5}BeCl_{4.5}OP_2$	$C_{38}H_{34}BeCl_6P_2$	$C_{38}H_{34}Cl_4P_2$	$C_{117.5}H_{102.5}Be_6Cl_{11.5}O_{11}P_6$
mw /g mol^{-1}	656.52	774.36	694.39	2386.50
a /Å	8.362(1)	14.044(1)	8.842(1)	23.221(1)
b /Å	19.295(1)	18.758(1)	26.783(1)	15.591(1)
c /Å	19.931(1)	14.200(1)	14.642(1)	32.561(2)
α /°	74.56(1)	90	90	90
β /°	89.37(1)	102.58(1)	101.67(1)	103.59(1)
γ /°	80.89(1)	90	90	90
crystal size /mm	0.28 × 0.15 × 0.1	0.28 × 0.11 × 0.05	0.42 × 0.05 × 0.04	0.24 × 0.23 × 0.11
volume /Å^3	3059.0(4)	3661.3(4)	3395.8(5)	11460(1)
Z	4	4	4	4
d_{calc} /g·cm^{-3}	1.426	1.405	1.358	1.383
crystal system	triclinic	monoclinic	monoclinic	monoclinic
space group	$P\bar{1}$ (Nr. 2)	$P2_1/c$ (Nr. 14)	$P2_1/c$ (Nr. 14)	$P2_1/c$ (Nr. 14)
diffractometer	IPDS II (Stoe)	IPDS II (Stoe)	IPDS II (Stoe)	IPDS II (Stoe)
radiation	Mo-K_α	Mo-K_α	Mo-K_α	Mo-K_α
temperature /K	100	193	100	100
μ /cm^{-1}	5.61	5.8	4.7	4.45
$2\theta_{max}$/°	56.84	52.17	52.64	52.04
index range	$-11 \le h \le 10$ $-25 \le k \le 25$ $-26 \le l \le 25$	$-17 \le h \le 17$ $-23 \le k \le 23$ $-16 \le l \le 17$	$-11 \le h \le 11$ $-33 \le k \le 33$ $-18 \le l \le 18$	$-28 \le h \le 28$ $-19 \le k \le 19$ $-40 \le l \le 37$
number of rflns collected	31828	49810	33643	94533
number of indep. rflns (R_{int})	15199 (0.1163)	7234 (0.1303)	6878 (0.1146)	22313 (0.3347)
number of observed rflns with $F_0 > 4\sigma(F_0)$	6858	3980	3470	6520
parameters	731	433	406	1020
absorption correction	numerical	numerical	numerical	numerical
structure solution	direct methods SIR-92[25]	direct methods SHELXS-97[26]	direct methods SIR-92[25]	direct methods SIR-92[25]
refinement against F^2	SHELXL-97[27]	SHELXL-97[27]	SHELXL-97[27]	SHELXL-97[27]
hydrogen atoms	calculated positions with common displacement parameter	calculated positions with common displacement parameter. H(1) and H(2) were refined free	calculated positions with common displacement parameter. H(1) and H(2) were refined free	calculated positions with common displacement parameter
R_1	0.0683	0.0535	0.0368	0.0974
wR_2 (all data)	0.1585	0.1153	0.0503	0.2568
max. electron density left/e·Å^{-3}	0.873	1.11	0.246	0.851

Table 2. Selected bond lengths /Å and angles /° of $(H_2C\{PPh_3\}_2)Cl_2{\cdot}CH_2Cl_2$ (**7**).

7			
C(1)–P(1)	181.3(3)	C(1)–P(2)	181.0(3)
C(1)–H(1)	102(2)	C(1)–H(2)	100(83)
P(1)–C(8)	179.7(3)	P(1)–C(14)	178.2(3)
P(1)–C(2)	179.0(3)	P(2)–C(32)	180.0(2)
P(2)–C(26)	179.6(3)	P(2)–C(20)	179.6(3)
P(1)–C(1)–P(2)	113.3(2)	P(1)–C(1)–H(1)	107(1)
P(2)–C(1)–H(1)	108(1)	P(1)–C(1)–H(2)	99(2)
P(2)–C(1)–H(2)	111(2)	H(1)–C(1)–H(2)	109(2)

transannular hydrogen bridge exist between H(1) and O(12) with O(1)···O(12) = 2.734(9) Å. For all beryllium atoms a tetrahedral coordination is achieved; Be(1), Be(3), and Be(4) are in a O_3Cl environment, Be(2) and Be(5) are O_4 coordinated and Be(6) is in a Cl_2O_2 environment. All OH groups act as bridging ligands and one in a μ_3-way, whereas the chlorine atoms are bonded in a terminal manner. Each molecule of **3** bridges two beryllium atoms; the four beryllium atoms Be(3) to Be(5) have contact to one oxygen atom, Be(1) to two oxygen atoms of **3** and Be(6) has no contact. The Be–OH bond lengths range from 1.57(2) to 1.72(1) Å; the three longest belong to those to O(1) bridging three beryllium atoms. A series of compounds are known with six membered BeO rings via bridging OH groups; the average Be–O bond lengths to the bridging OH groups range between 1.586 and 1.593 Å. The other two coordination sites at the three ring beryllium atoms are occupied by O or N donors.[22] The coordination to the beryllium atoms has remarkable influence on the structural parameters of **3**. As expected the mean C–C bond length decreases to 1.46(1) Å from 1.494(3) Å in free **3** and the mean C–O distance increases by about 0.02 Å upon coordinating to

Table 3. Selected bond lengths /Å and angles /° of one of the two independent molecules of $[Ph_3PCH_2P(OBeCl_3)Ph_2]{\cdot}0.75CH_2Cl_2$ (**5**).

5			
Be(1)–O(1)	1.657(7)	Be(1)–Cl(1)	2.021(6)
Be(1)–Cl(2)	2.037(6)	Be(1)–Cl(3)	2.046(6)
O(1)–P(1)	1.498(3)	C(1)–P(2)	1.803(5)
C(1)–P(1)	1.841(5)	C(1)–H(11)	0.9900
C(1)–H(11)	0.9900	P(1)–C(2)	1.791(5)
P(1)–C(8)	1.811(5)	P(2)–C(14)	1.793(5)
P(2)–C(20)	1.796(5)	P(2)–C(26)	1.793(5)
O(1)–Be(1)–Cl(1)	106.3(3)	O(1)–Be(1)–Cl(2)	109.1(4)
Cl(1)–Be(1)–Cl(2)	112.0(3)	O(1)–Be(1)–Cl(3)	111.4(3)
Cl(1)–Be(1)–Cl(3)	110.9(3)	Cl(2)–Be(1)–Cl(3)	107.2(3)
P(1)–O(1)–Be(1)	143.9(3)		
P(1)–C(1)–P(2)	118.6(3)	P(2)–C(1)–H(11)	107.7
P(1)–C(1)–H(11)	107.7	P(2)–C(1)–H(11)	107.7
P(1)–C(1)–H(11)	107.7	H(11)–C(1)–H(11)	107.1
O(1)–P(1)–C(2)	114.4(2)	O(1)–P(1)–C(8)	110.9(2)
C(2)–P(1)–C(8)	111.0(2)	O(1)–P(1)–C(1)	110.7(2)
C(2)–P(1)–C(1)	100.9(2)	C(8)–P(1)–C(1)	107.3(2)
C(26)–P(2)–C(14)	111.3(2)	C(26)–P(2)–C(20)	109.6(2)
C(14)–P(2)–C(20)	106.9(2)	C(26)–P(2)–C(1)	110.8(2)
C(14)–P(2)–C(1)	109.9(2)	C(20)–P(2)–C(1)	107.1(2)

Table 4. Selected bond lengths /Å and angles /° of $(H_2C\{PPh_3\}_2)[BeCl_4]{\cdot}CH_2Cl_2$ (**6**).

6			
C(1)–P(1)	1.814(4)	C(1)–P(2)	1.819(4)
C(1)–H(1)	0.87(4)/ 102(2)	C(1)–H(2)	1.06(4)
P(1)–C(8)	1.799(4)	P(1)–C(14)	1.802(4)
P(1)–C(2)	1.797(4)	P(2)–C(32)	1.797(4)
P(2)–C(26)	1.784(4)	P(2)–C(20)	1.797(4)
Cl(1)–Be(1)	2.072(5)	Cl(2)–Be(1)	1.992(6)
Cl(3)–Be(1)	2.067(5)	Cl(4)–Be(1)	2.046(6)
C(1)···Cl(1A)	3.578(4)	C(1)···Cl(3)	3.550(4)
P(1)–C(1)–P(2)	112.0(2)	P(1)–C(1)–H(1)	103(3)
P(2)–C(1)–H(1)	109(3)	P(1)–C(1)–H(2)	110(2)
P(2)–C(1)–H(2)	103(2)	H(1)–C(1)–H(2)	109(4)
Cl(1)–Be(1)–Cl(2)	110.0(3)	Cl(1)–Be(1)–Cl(3)	107.6(2)
Cl(1)–Be(1)–Cl(4)	108.9(3)	Cl(2)–Be(1)–Cl(3)	109.9(3)
Cl(2)–Be(1)–Cl(4)	113.1(2)	Cl(3)–Be(1)–Cl(4)	107.6(3)
C(1)–H(1)···Cl(1A)	176(3)	C(1)–H(2)···Cl(3)	164(3)

the beryllium atoms. As a consequence of the electron withdrawing effect of the beryllium atoms the mean value of the P–C bond lengths has increased from 1.718 in **3** to 1.744 in **8**, which means that the backbonding of the π electron pair into $PC_{Ph}\sigma^*$ orbitals has decreased in favor of an increasing C–C double bond character.[11] The coordination of **3** leads to three six-membered BeOCOBeO rings and the CO_2 bite angle has only slightly decreased from 117.7(2)° in **3** to a mean value of 113.3(9)°. The majority of angles at the beryllium atoms are not far away from the tetrahedral angle ranging between 106 and 114°.

Table 5. Selected bond lengths /Å and angles /° of $[Be_6(OH)_6Cl_5(O_2C_2\{PPh_3\}_2)_3]Cl$ (**8**).

8			
Be(1)–O(1)	1.67(1)	Be(2)–O(1)	1.71(1)
Be(5)–O(1)	1.72(1)	Be(1)–O(2)	1.60(1)
Be(1)–O(9)	1.64(1)	Be(1)–Cl(1)	2.04(1)
Be(2)–O(4)	1.57(2)	Be(2)–O(10)	1.59(2)
Be(2)–O(3)	1.66(1)	Be(3)–O(4)	1.64(2)
Be(3)–O(11)	1.64(1)	Be(3)–O(5)	1.66(2)
Be(3)–Cl(2)	2.01(1)	Be(4)–O(7)	1.64(2)
Be(4)–O(11)	1.64(1)	Be(4)–O(6)	1.66(2)
Be(4)–Cl(3)	2.03(1)	Be(5)–O(11)	1.59(1)
Be(5)–O(7)	1.61(2)	Be(5)–O(8)	1.62(1)
Be(6)–O(11)	1.59(2)	Be(6)–O(10)	1.60(1)
Be(6)–Cl(4)	2.02(1)	Be(6)–Cl(5)	2.15(2)
O(2)–C(2)	1.29(1)	O(3)–C(2)	1.25(1)
O(5)–C(40)	1.30(1)	O(6)–C(40)	1.27(1)
O(8)–C(78)	1.28(1)	O(9)–C(78)	1.28(1)
C(1)–C(2)	1.46(1)	C(39)–C(40)	1.45(1)
C(77)–C(78)	1.47(1)	C(1)–P(2)	1.732(9)
C(1)–P(1)	1.745(9)	C(39)–P(4)	1.75(1)
C(39)–P(3)	1.756(9)	C(77)–P(5)	1.728(9)
C(77)–P(6)	1.75(1)		
O(3)–C(2)–O(2)	113.6(8)	O(5)–C(40)–O(6)	112.3(9)
O(9)–C(78)–O(8)	114(1)	C(2)–O(2)–B(1)	130.3(7)
C(2)–O(3)–B(2)	117.7(7)	C(40)–O(5)–B(3)	111.9(8)
C(40)–O(6)–B(4)	115.4(8)	C(78)–O(8)–B(4)	119.0(8)
C(78)–O(9)–B(1)	112.1(8)		

4 Conclusion and Outlook

The coordination chemistry of beryllium compounds is less developed in comparison to those of its neighboring elements.[15] The small seize and strongly polarizing character of the Be^{2+} ion is the basis of its strong oxophilicity. **2** and **3** are equipped with hard oxygen atoms and should be prone to coordinate at the beryllium atom. However, the lack of getting suitable crystals in most cases prevented characterization of the simple addition compounds. In general for **2** and **3** the coordination modes **A**, **B**, **C** (**3**) and **I** to **IV** (**2**) are to be expected (Scheme 3). Whereas compounds of type **A** and **B** were reported previously by us, mode **C** is realized in the cluster complex **8** described in this contribution (Scheme 4). The neutral complex **5** is represented by coordination mode **III** but in which **M** at the carbon atom is replaced by hydrogen. In the case of **2** examples for coordination mode **IV** are missing so far.

The reaction of **3** with Lewis acids in halogenated hydrocarbons undergoes a competitive reaction between additionand deprotonation of the solvent to give the cation $(H{\leftarrow}\mathbf{1})^+$. ^{31}P NMR experiments on solutions of **3** in DCM or 1,2-dichloroethane showed that the signal of **3** at δ = 14 ppm disappeared within some hours in favor of the signal of the cation. In the case of 1,2-dichloroethane as solvent a further competitive reaction was observed between formation of the cation and a substitution reaction resulting in $ClCH_2CH_2OC(O)C(PPh_3)_2$.[23] The first results from the reaction of **2** and **3** with beryllium halides are very promising and can be seen as a challenge for further studies in this area.

5 Experimental Section

All operations were carried out under an argon atmosphere in dried and degassed solvents using Schlenk techniques. The solvents were thoroughly dried and freshly distilled prior to use. The IR spectra were run on a Nicolet 510 spectrometer in Nujol mull (The Nujol mull bands are omitted). For the ^{31}P NMR spectra we used the instrument Bruker AC 300. The carbodiphosphorane $C(PPh_3)_2$ (**1**) was prepared according to a modified literature procedure;[24] The syntheses of hydrolysis product **2**[1,9] and the CO_2 adduct **3**[6] were described recently. $BeCl_2$ was prepared from the elements and $(PPh_4)[Be_2Cl_6]$ was obtained from $BeCl_2$ and $(PPh_4)Cl$.[14]

Reaction of 2 with $BeCl_2$: A mixture of **2** (0.16 g, 0.33 mMol) and $BeCl_2$ (0.06 g, 0.07 mMol) in DCM (about 4 mL) was mechanically stirred for 24 h at room temperature. The solution was separated from some insoluble material by filtration. The ^{31}P NMR spectrum of the solution showed two doublets at δ = 37.6 and 18.5 ppm (^2J(P,P) = 21.5 Hz), which indicates the formation of an addition compound $Cl_2Be{\leftarrow}$**2** (**4**). No suitable crystals for an X-ray analysis were formed upon layering the solution with *n*-pentane. Removal of the solvent and taking up the residue in DMSO gave a solution; the formation of the cation $[Ph_3PCH_2P(O)Ph_2]^+$ (H←**2**)$^+$ was established by ^{31}P NMR spectroscopy.

In a second run attempts were made to get larger crystals by very slow diffusion of *n*-pentane into a solution of a mixture of **2** (0.23 g, 0,5 mMol) and $BeCl_2$ (0.05 g, 0.6 mMol) in DCM. Thus, in a three necked Schlenk tube a clear solution from one neck was transferred into the second one; the third one was supplied with *n*-pentane. In the course of several weeks crystals separated, which, however, were not suitable for an X-ray analysis. The ^{31}P NMR spectrum of the supernatant solution showed three sets of AX signals; set 1 at 34.7, 18.8 (*J*(P,P) = 21.5 Hz), set 2 at 32.7, 18.7 (*J*(P,P) = 23.3 Hz) and set 3 at 22.7, 27.2 (^2J(P,P) = 14.3 Hz) ppm; the latter could be assigned to the cation $[Ph_3PCH_2P(O)Ph_2]^+$ (H←**2**)$^+$.

Reaction of 2 with $(PPh_4)[Be_2Cl_6]$: A mixture of **2** (0.19 g, 0.4 mMol) and $(PPh_4)[Be_2Cl_6]$ (0.18 g, 0.2 mMol) was dissolved in DCM (about 4 mL) and stirred mechanically for about 30 min. Additionally to the signal of the cation $(PPh_4)^+$ at δ = 22.9 ppm the ^{31}P NMR spectrum of the reaction mixture shows two sets of signals for the phosphorus atoms: set 1 with 36.05, 19.65 ppm, *J*(P,P) = 17.9 Hz and set 2 with 31.45, 18.77 ppm, *J*(P,P) = 21.5 Hz in a 1:2 ratio according to two different addition compounds between **2** and $BeCl_3^-$. The DCM solution was layered with *n*-pentane. An oil was formed from which crystals of $[Ph_3PCH_2P(OBeCl_3)Ph_2]{\cdot}0.75CH_2Cl_2$ (**5**) separated. The ^{31}P NMR of the supernatant solution showed that the signals due to set 1 have disappeared. **IR** (Nujol, cm^{-1}): 1588 m, 1464 m, 1438 s, 1360 m, 1270 w, 1164 vs, 1113 vs, 996 m, 819 s,784 s, 730 vs, 688 vs, 617 w, 596 vs, 501 m, 496 m.

Reaction of 3 with $BeCl_2$: A mixture of Compound **3** (1.20 g, 2.07 mmol) and $BeCl_2$ (0.175 g, 2.13 mmol) in DCM (about 8 mL) was stirred at room temperature for 1 day. The ^{31}P NMR of the solution showed a signal at δ = 21.2 ppm. The solvent was removed in vacuo to give an oil without forming crystals. The oil was again dissolved in DCM; in the ^{31}P NMR two signals were detected at δ = 20.7 and 19.0 ppm in a x:y ratio (PeDeh1). Layering with *n*-pentane produced crystals of $(H_2C\{PPh_3\}_2)[BeCl_4]{\cdot}CH_2Cl_2$ (**6**). **^1H NMR** ($CDCl_3$): 7.2 to 8.2 (m, Ph), 8.44 (t, CH_2, *J*(H,P = 15,6 Hz) ppm. **^{31}P NMR** (DCM): 19.2 ppm. **IR** (Nujol, cm^{-1}): 1586 m, 1483 m, 1441 s, 1337 m, 1316 w, 1162 m, 1117 w, 1192 w, 1171 w, 1111 s, 995 m, 810 m, 801 s, 745 vs, 723 m, 696 m, 687 s, 544 s, 511 s, 500 s, 488 m, 480 m. The solution was decanted from the crystals followed by layering with *n*-pentane to give needle-like crystals of $(H_2C\{PPh_3\}_2)Cl_2{\cdot}CH_2Cl_2$ (**7**).

The oily material, separated from the crystals of **7**, still contained an addition compound with **3** as shown by IR spectroscopy. **IR** (neat, cm^{-1}): 1547 s, 1544 sh, 1483 m, 1437 s, 1380 vs, 1316 w, 1188 w, 1103 s, 1074 w, 1026 w, 997 m, 932 w, 795 m, 747 s, 720 s, 689 s, 525 s. The oil was again dissolved in DCM, layered with *n*-pentane, causing again separation of an oily material instead of crystals. The mixture was allowed to stand for about two month at room temperature. After that time a couple of colorless crystals were detected, which turned out to be the cluster compound $[Be_6(OH)_6Cl_5(O_2C_2\{PPh_3\}_2)_3]$-$Cl{\cdot}3.25CH_2Cl_2$ (**8**). The OH groups probably originated from contact to humidity introduced by a leaking stopcock during this period. **^{31}P NMR:** 20.97 to 20.27 (broad), 19.94 ppm. **IR** (Nujol, cm^{-1}): 3680 w (OH), br, 3055 w, 1549 s, 1542 sh, 1483 w, 1437 s, 1385 s, 1263 w, 1105 s, 1074 w, 1051 w, 1062 w, 999m, 934 w, br, 833 m, 814 m, 745 s, 733 s, 723 s, 689 s, 525 m, 511 m, 502 m.

Reaction of 3 with $(PPh_4)_2[Be_2Cl_6]$: A mixture of **3** (0.03 g, 0.04 mMol) and $(PPh_4)_2[Be_2Cl_6]$ (0.08 g, 0.2 mMol) was dissolved in DCM (about 3 mL) and stirred mechanically for about 11 h. The ^{31}P NMR spectrum of the solution showed signals at δ = 22.2 and 19.0 ppm. No suitable crystals were obtained upon layering with *n*-pentane. The solvent was removed in the residue dissolved in 1,2-dichloroethane and layered with *n*-pentane. Needle-like crystals formed, which turned out to be the salt **7**.

Crystallographic data for the structures have been deposited with the Cambridge Crystallographic Data Centre, 11 Union Road, Cambridge CB21EZ. Copies of the data can be obtained on quoting the depository numbers CCDC-830895 (**5**), CCDC -830896 (**6**), CCDC -830897 (**7**), CCDC -830898 (**8**) (Fax: +44-1123-336-033; E-mail: deposit@ccdc.cam.ac.uk).

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