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The Reaction of $BeCl_2$ with Carbodiphosphorane $C(PPh_3)_2$; Experimental and Theoretical Studies

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In Memory of Professor Kurt Dehnicke

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Abstract. The use of 2-Br-fluorobenzene as the solvent permitted the isolation of the addition compound $[Cl_2Be(C\{PPh_3\}_2)]$ (**5**) from the reaction of the carbodiphosphorane **1** (carbon) with $BeCl_2$ featuring a three coordinate beryllium atom. In other solvents such as THF, DCM, etc. deprotonation occurs with formation of the cations $(HC\{PPh_3\}_2)^+$ or $(H_2C\{PPh_3\}_2)^{2+}$. Compound **5** was characterized by an X-ray diffraction analysis. The analysis of the bonding situation in $Cl_2Be{\leftarrow}\mathbf{1}$ reveals that the orbital donation comes mainly from the σ lone-pair orbital of **1**, whereas the π donation is rather weak. However, the $Cl_2Be{\leftarrow}\mathbf{1}$ π donation appears strong enough to make the donation of a second donor species **1** unfavorable. The calculation of $\mathbf{1}{\rightarrow}Cl_2Be{\leftarrow}\mathbf{1}$ shows that the latter complex is higher in energy than $\mathbf{1}{\rightarrow}Cl_2Be$ and free **1**. The carbodiphosphorane may bind, albeit weakly, a second $BeCl_2$ species in the complex $Cl_2Be{\leftarrow}\mathbf{1}{\rightarrow}BeCl_2$. The bond dissociation energies for the first and second $BeCl_2$ fragments are D_e = 31.8 $kcal{\cdot}mol^{-1}$ and 7.0 $kcal{\cdot}mol^{-1}$. The dimerization of $Cl_2Be{\leftarrow}\mathbf{1}$ is energetically slightly endoenergetic.

1. Introduction

It has recently been shown that the bonding situation in hexaphenylcarbodiphosphorane $C(PPh_3)_2$ (**1**),[1] which has a bent equilibrium arrangement with a P–C–P angle of 131.7°,[2] is best described in terms of donor-acceptor interactions between the phosphane ligands and a naked carbon(0) atom in the ^1D state (Scheme 1). The bonding interactions give rise to two electron lone-pair orbitals at the divalent carbon(0) atom.[3] The donor-acceptor model L→C←L for **1** ($L = PPh_3$) provides a straightforward explanation for the increase of the bending angle in carbonylcarbophosphorane $C(CO)(PPh_3)_2$ (**2**, bending angle 145.6°)[4] and carbon suboxide C_3O_2 (**3**, bending angle 156.5°)[5] because the phosphane ligands are substituted by the better π-acceptor ligand CO.[6] Carbon suboxide[7] is usually written with double bonds O=C=C=C=O but should better be considered as dicarbonyl complex of a naked carbon atom in the excited ^1D state OC→C←CO. The donor-acceptor model L→C←L for **1** led to the prediction that hitherto unknown carbodicarbenes $C(NHC)_2$ (**4**, NHC = N-heterocyclic carbene), which feature unusual carbon→carbon donor-acceptor bonds should be stable compounds.[3b] The prediction was quickly verified by the synthesis and X-ray structure analysis of the first carbodicarbenes by *Bertrand*[8] and by *Fürstner*.[9] The experimentally observed bending angle of 134.8° for **4**, which is similar to the value for **1** is in agreement with the finding that the ligands NHC and PR_3 bind in a similar fashion to a Lewis acid.[10] The term carbone was suggested for compounds CL_2,[11] which due to the presence of two electron lone pairs have very large first and second proton affinities,[12] and which exhibit a chemical behavior that is distinctively different from carbenes CR_2, which have only one lone pair.[13]

Carbodiphosphoranes are versatile ligands, which are employed in a variety of adducts.[14] The presence of two electron lone pairs makes **1** a powerful Lewis base, which forms strongly bonded complexes with various main group Lewis acids[15] particularly group 13 compounds[16] and with transition metal Lewis acids,[17] where one pair of electrons is employed in donor-acceptor bonding (compounds **A** in Scheme 1). Recently, compounds of the type $\mathbf{1}{\rightarrow}M{\leftarrow}\mathbf{1}$ (M = Cu^+, Ag^+, Hg^{2+}) were also reported.[18] The presence of two lone pairs in **1** was used for the isolation of complexes, where both pairs of electrons coordinate to two gold[19] or two boron[20] atoms as shown in **B** (Scheme 1). The extraordinary donor strength of **1** has even been used for C–H activation in the reaction with $[(cod)PtX_2]$.[21]

An intriguing question, which has so far not been studied concerns the reaction of the double Lewis base **1** with a double

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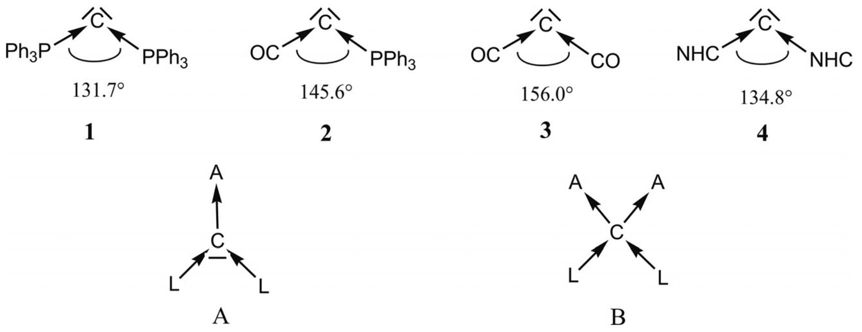

Scheme 1. Schematic representation of the bonding situation in the carbones **1**–**4** showing the experimental bending angles at the divalent carbon(0) atom. Chemical bonding in complexes **A** and **B**, where the carbone binds to one Lewis acid (**A**) and to two Lewis acids (**B**).

Lewis acid such as $BeCl_2$. The chemistry of beryllium compounds was not explored very much, mainly because beryllium and its compounds are regarded as highly toxic.[22] Recent theoretical studies have shown that $BeCl_2$ is a rather strong Lewis acid.[23] Although beryllium is less electronegative than boron, compound $BeCl_2$ strongly attracts electron donors because it has two formally vacant valence orbitals, whereas BCl_3 has only one. Herein we report on the results of the reaction of $BeCl_2$ with **1** and on theoretical studies of various complexes of **1** with $BeCl_2$.

2. Experimental Studies

One disadvantage of $X_3E\leftarrow\mathbf{1}$ complexes (X_3E = group 13 compound) is the fact that they are insoluble in nonpolar solvents like toluene or benzene and they are unstable in halogenated hydrocarbons, THF, DME, or DMSO. In most cases proton abstraction from the solvents occurs to give the cations $(HC\{PPh_3\}_2)^+$ or $(H_2C\{PPh_3\}_2)^{2+}$. This feature complicates spectroscopic characterization in solution or crystal growth for X-ray analyses. Thus, we were restricted to nonpolar solvents such as toluene or benzene in spite of the fact that the beryllium salt is insoluble in these solvents. If solid $BeCl_2$ was added to a suspension of **1** in toluene (it totally dissolves only in hot toluene) a colorless microcrystalline precipitate is formed. From the IR spectrum of the solid limited structural information could be deduced but the formation of the cation $(HC\{PPh_3\}_2)^+$ could be excluded because of the lack of the characteristic bands at 999 s, 1011 m, 1030 w cm^{-1}.[21a] We suppose that the adduct ($Cl_2Be\leftarrow\mathbf{1}$) has formed but also its dimeric nature cannot be excluded according to the electron demand of the beryllium atom. The difficulties to obtain crystals prompted us to look for alternative solvents without any donor properties or tendencies to transfer a proton to **1**. Surprisingly, we were successful when we switched to 2-Br-fluorobenzene as the solvent and $[Cl_2Be(C\{PPh_3\}_2)]$ (**5**) was obtained as colorless crystals in high yield. A 1:1 mixture of $BeCl_2$ and **1** was heated for one minute in this solvent; layering of the resulting tan solution with *n*-pentane produced colorless crystals within one week, suitable for an X-ray analysis. Apparently, the solvent used is polar enough to dissolve **5** and puts up resistance to any abstraction of H*X*. **5** is the first addition compound of **1** with a group 2 Lewis acid. In spite of an electron deficiency at the beryllium atom the compound is monomeric containing a three coordinate beryllium atom. Such compounds are rare and their existences are indebted to sterically encumbered ligands and the small size of the beryllium atom preventing dimerization [Equation (1)]

$$\mathbf{1} + BeCl_2 \rightarrow Cl_2Be\leftarrow C(PPh_3)_2\ (\mathbf{5}) \qquad (1)$$

The IR spectrum of **5** between 3000 and 400 cm^{-1} is mainly governed by the frequencies of the carbodiphosphorane ligand; however, there is a strong band at 890 cm^{-1}, which has not been found in the spectrum of the cation $(HC\{PPh_3\}_2)^+$ or of other addition compounds of **1** that can be assigned to the ν(Be–C) vibration.[24]

The addition compound **5** crystallizes without incorporating solvent molecules and the molecular structure is shown in Figure 1 and Figure 2. The sum of the angles at Be and at C(1) each amounts to 360°, which indicates perfect trigonal planar coordination at both atoms. The $BeCl_2$ plane is rotated by 44° with respect to the CP_2 plane. The average Be–Cl bond length is somewhat longer (1.953 Å) than those observed in the Be–N adduct $[Cl_2Be(N\{SiMe_3\}PeEt_3)]$ with 1.927 Å[25] and in the Be–Pt adduct $[Cl_2Be\text{-}Pt(PCy_3)_2]$ with 1.922 Å.[26] Both compounds are the only examples with a three coordinate $BeCl_2$ base adduct so far. Similar compounds with a Cl_2Be–C moiety as in **5** were not reported. If $BeCl_2$ is embedded in a four-membered ring, quite longer Be–Cl bond lengths of 2.018 Å were found.[27]

In order to grow also crystals from the toluene precipitate to clear up its identity with **5** the suspension was filtered immediately after adduct formation and the filtrate was allowed to stand for a couple of time. Some microcrystalline powder separated with time and after months some larger crystals have formed but which turned out to be the salt $(Ph_3PMe)Cl$ ·0.25toluene (**6**). The origin of **6** is unclear as yet; there was no sign for the presence of **6** as impurity in **1**. For further characterization the initial toluene precipitate was treated with several polar solvents. It dissolves readily in DMSO and the ^{31}P NMR spectrum exhibits only one singlet at 21.0 ppm, which was assigned to the cation $(HC\{PPh_3\}_2)^+$. Layering of the DMSO solution with toluene gave some colorless crystals which turned out to be the salt $[Be(DMSO)_4]Cl_2$ (**7**) according to an X-ray analysis;[28] no further crystalline material was

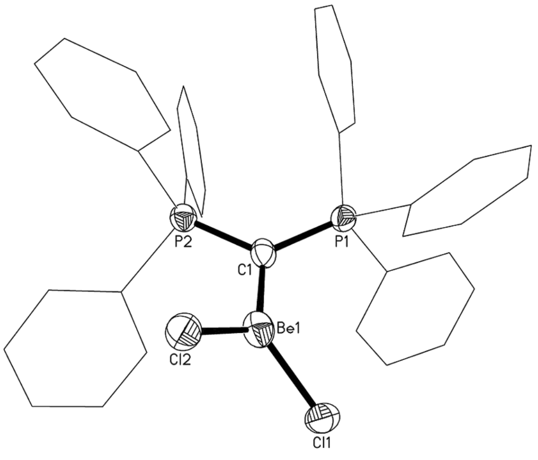

Figure 1. Molecular structure of $[Cl_2Be(C\{PPh_3\}_2)]$ (**5**) showing the atom numbering scheme. The ellipsoids are drawn at a 40 % probability level. The hydrogen atoms at the phenyl rings are omitted for clarity. Selected bond lengths /Å and angles /°: Be(1)–C(1) 1.742(9), Be(1)–Cl(1) 1.944(7), Be(1)–Cl(2) 1.961(7), C(1)–P(2) 1.697(4), C(1)–P(1) 1.711(5); C(1)–Be(1)–Cl(1) 124.8(4), C(1)–Be(1)–Cl(2) 120.3(4), Cl(1)–Be(1)–Cl(2) 114.9(4), P(2)–C(1)–P(1) 123.4(3), P(2)–C(1)–Be(1) 115.2(4), P(1)–C(1)–Be(1) 121.2(3).

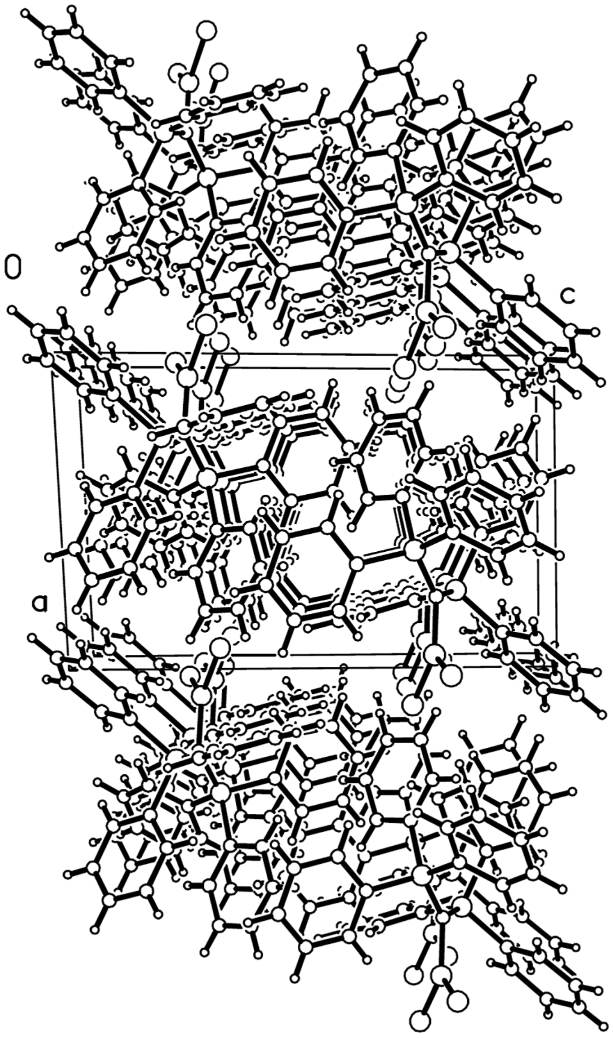

Figure 2. Unit cell of **5** viewed down [100] with several asymmetrical units of **5**.

obtained. The formation of **7** reflects the high affinity of Be^{2+} to oxygen.

The precipitate does not dissolve in THF but contacts with dry THF changed the IR spectrum and bands of the cation $(HC\{PPh_3\}_2)^+$ appeared. When dissolved in CH_2Cl_2 or DMF a clear solution was obtained and only the cation $(HC\{PPh_3\}_2)^+$ at 20.6 ppm was identified spectroscopically. Similar results are obtained upon dissolving the precipitate in acetone or pyridine. The precipitate was also dissolved in tetramethylguanidine $[HN=C(NMe_2)_2]$; the ^{31}P NMR spectrum of the solution shows two signals at 20.4 and 24.0 ppm in a 1:0.3 ratio, respectively. The high field signal was again assigned to the cation, whereas the nature of the other one remained unexplored so far. The results confirm our earlier findings that with $M \leftarrow \mathbf{1}$ (*M* = group 13 or group 12 Lewis acids) adducts in polar and halogenated solvents extraction of a proton takes place. The strong polarizing effect of the small Be^{2+} ion may enforce this reaction pathway.

Addition of freshly dried DME (over potassium) to the precipitate gave a suspension, from which upon standing colorless needle-like crystals separated, which were found to be the salt $(H_2C\{PPh_3\}_2)Cl_2 \cdot DME$ (**8**). The supernatant solution exhibits a signal in the ^{31}P NMR spectrum at $\delta = 20.8$ ppm, which was assigned to the cation $(HC\{PPh_3\}_2)^+$, the same shift was found upon dissolving the residue from the DME solution in DMSO or CH_2Cl_2. We suppose that in solution dissociation occurs of the dication to give the monocation according to Equation (2).

The IR spectrum of **8** from DME does not show the characteristic set of bands (999 s, 1011 m, 1030 w cm^{-1}) due to the cation $(HC\{PPh_3\}_2)^+$ but those of the coordinated solvent molecule. From a series of compounds with the dication $(H_2C\{PPh_3\}_2)^{2+}$ [and the counterions Cl^-, $[BF_4]^-$, $[BeCl_4]^{2-}$, etc.] only one single medium to weak band is detected in this region at 997 cm^{-1}.

$$(H_2C\{PPh_3\}_2)Cl_2 \rightarrow (HC\{PPh_3\}_2)Cl + HCl \qquad (2)$$

The experimental results prompted us to carry out theoretical studies on $(Cl_2Be \leftarrow \mathbf{1})$ (**5**) and on the doubly coordinated adducts $(Cl_2Be \leftarrow \mathbf{1} \rightarrow BeCl_2)$ and $(\mathbf{1} \rightarrow BeCl_2 \leftarrow \mathbf{1})$. We also studied the dimer $\mathbf{5}_2$, where two monomers **5** are bonded to each other by beryllium–chlorine bridges.

3. Theoretical Studies

We optimized the arrangement of $(Cl_2Be \leftarrow \mathbf{1})$ (**5**) at the BP86/SVP level (see method section for details). The calculated structure is shown in Figure 3a. The most important bond lengths and angles are given in Table 1 together with the experimental values. The comparison between the theoretical and experimental data shows a very good agreement. The deviations between the two sets of data are within the error range of both methods but the differences will also be caused by intermolecular forces in the solid state. The calculated (1.782 Å) and experimental (1.742(9) Å) Be–C bond length is

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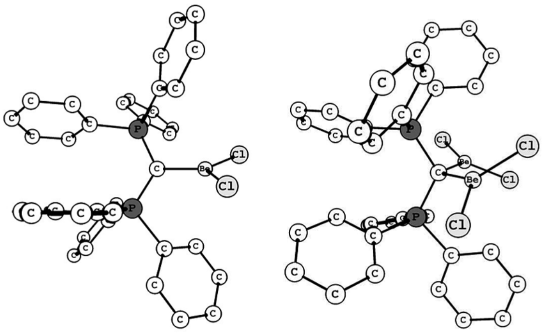
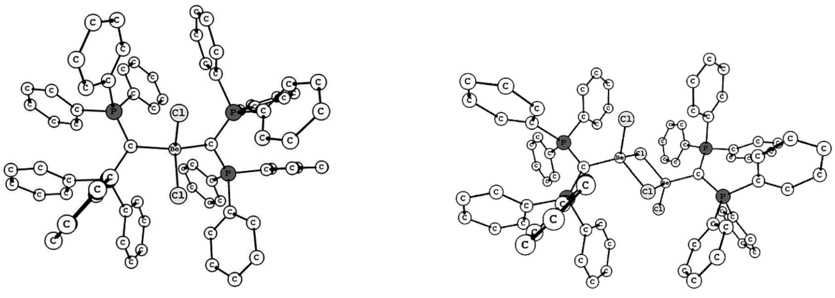


(a) Cl$_2$Be←**1** (**5**)

(b) Cl$_2$Be←**1**→BeCl$_2$



(c) **1**→BeCl$_2$←**1**

(d) (Cl$_2$Be←**1**)$_2$ (**5**)$_2$

Figure 3. Optimized geometries (BP86/SVP) of the complexes (a) Cl$_2$Be←**1** (**5**), (b) Cl$_2$Be←**1**→BeCl$_2$, (c) (**1**→BeCl$_2$←**1**) and (d) (Cl$_2$Be←**1**)$_2$ (**5**)$_2$. The most important bond lengths and bond angles are given in Table 1.

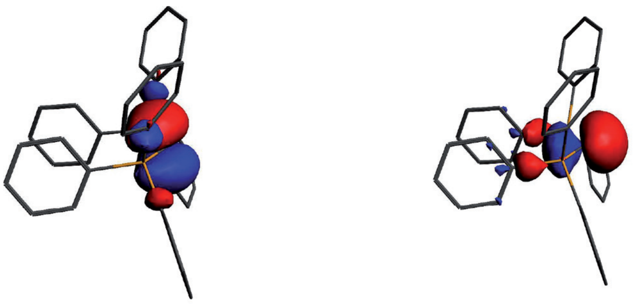
in the range of Be–*Ar* single bonds (*Ar* = C_6H_3-2,6-Mes$_2$), which were recorded in various three coordinate *Ar*Be*X* base adducts.[29] Thus, the Be–C(1) bond in **5** suggests that a double-bond character, which would come from significant Be←C π donation is not very large. This may be due to the unfavorable overlap of the p(π) orbitals of the beryllium and carbon atoms in the twisted conformation about the C–Be bond, which is caused by the steric interaction of the chlorine atoms with the phenyl groups. The calculated bond dissociation energy (BDE) of the Cl$_2$Be←**1** bond at BP86/TZVPP//BP86/SVP is D_e = 42.9 kcal·mol^{-1}. This is significantly higher than the calculated BDE of Cl$_2$Be←NH$_3$ which is only 27.4 kcal·mol^{-1}.[23b] The theoretical BDE of Cl$_2$Be←**1** is also much higher than the calculated value for the complex Cl$_2$Be←PPh$_2$(CH$_2$PPh$_2$) (D_e = 24.3 kcal·mol^{-1}),[23c] which indicates the large donor strength of **1**.

Figure 4 shows the two highest lying occupied orbitals of **1** and the two lowest lying vacant orbitals of BeCl$_2$. It becomes obvious that the π lone-pair HOMO and the σ lone-pair HOMO-1 of **1** are perfectly suited for electron donation in to the vacant π LUMO and the σ LUMO-1 of BeCl$_2$. We analyzed the nature of the (Cl$_2$Be←**1**) (**5**) donor-acceptor interactions with the EDA (Energy Decomposition Analysis) in order in quantitatively estimate the strength of the σ and π donation from carbodiphosphorane to BeCl$_2$. To this end we optimized the arrangement of **5** with enforced C_s symmetry, where the P–C–P and Cl–Be–Cl planes are coplanar. Table 2 gives the numerical results of the EDA calculations. The total interaction energy ΔE_{int} between the donor and acceptor fragments with the frozen arrangement of the complex amounts to –62.4 kcal·mol^{-1}. The electrostatic term ΔE_{elstat} contributes 55.7 %, while the orbital interactions ΔE_{orb} contributes 44.3 % to the total attraction. The latter term comes mainly from the Cl$_2$Be←**1** σ donation, which provides 89 % of the ΔE_{orb} term (Table 2). This means that the donation of the π lone-pair HOMO of **1** in **5**, which contributes only 11.0 % to ΔE_{orb} is not very strong. This is supported by the shape of the HOMO of the complex Cl$_2$Be←**1**. Figure 4e shows that the latter orbital still has the character of a π lone-pair orbital, which is mainly located at the carbon donor atom of **1**.

The analysis of the Cl$_2$Be←**1** donor-acceptor bond in **5** shows that the second electron lone pair of **1** is hardly involved in the binding interactions and may thus be available for bonding to a second BeCl$_2$ species. Figure 3b shows the optimized arrangement of Cl$_2$Be←**1**→BeCl$_2$. The calculated bond lengths of the C–Be bonds in the latter compound (1.875 Å and 1.880 Å, Table 1) are significantly longer than in **5** (1.782 Å). The same holds for the C–P bonds, which are calculated to be much longer in Cl$_2$Be←**1**→BeCl$_2$ (1.809 Å and 1.811 Å) than in **5** (1.720 Å and 1.722 Å). The theoretically predicted bond lengths suggest that the donor-acceptor bonds of the BeCl$_2$ molecules in the former complex are much

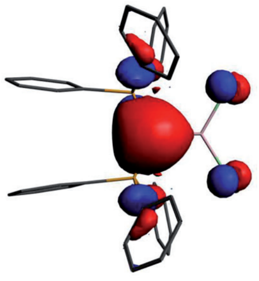
Table 1. Calculated (BP86/SVP) bond lengths d(A–B) /Å bond angles α(A–B–C) /° and interplanar angles τ /° of the investigated complexes. The values in parentheses refer to experimental data.

	$\mathrm{Cl_2Be}\leftarrow\mathbf{1}$ (**5**)	$\mathrm{Cl_2Be}\leftarrow\mathbf{1}\rightarrow\mathrm{BeCl_2}$	$\mathbf{1}\rightarrow\mathrm{BeCl_2}\leftarrow\mathbf{1}$	$(\mathrm{Cl_2Be}\leftarrow\mathbf{1})_2$ $(\mathbf{5})_2$
d(Be–Be)				3.006
d(Be–C)	1.782 (1.742)	1.875–1.880	1.965–2.020	1.819–1.823
d(Be–Cl)	1.955–1.970 (1.944–1.961)	1.935–1.965	2.056–2.080	2.033–2.050
d(Be–$\mathrm{Cl_{int}}$)				2.132–2.203
d(C--P)	1.720–1.722 (1.697–1.711)	1.809–1.811	1.724–1.750	1.724–1.733
α(Cl–Be–Cl)	119.0 (114.9)	116.0–116.8	106.9	91.5–92.4
α(P–C–P)	123.9 (123.4)	121.7	115.6–121.6	120.8–121.5
τ(P–C–P plane / Cl–Be–Cl plane)	58.2 (44)			
τ(C–Be–Cl plane / $\mathrm{Cl_{int}}$–Be–$\mathrm{Cl_{int}}$ plane)				89.0–89.6



(a) HOMO (**1**) (b) HOMO-1 (**1**)

(c) LUMO ($\mathrm{BeCl_2}$) (d) LUMO-1 ($\mathrm{BeCl_2}$)



(e) HOMO (**5**)

Figure 4. Shape of the frontier orbitals of **1**, $\mathrm{BeCl_2}$, and **5**.

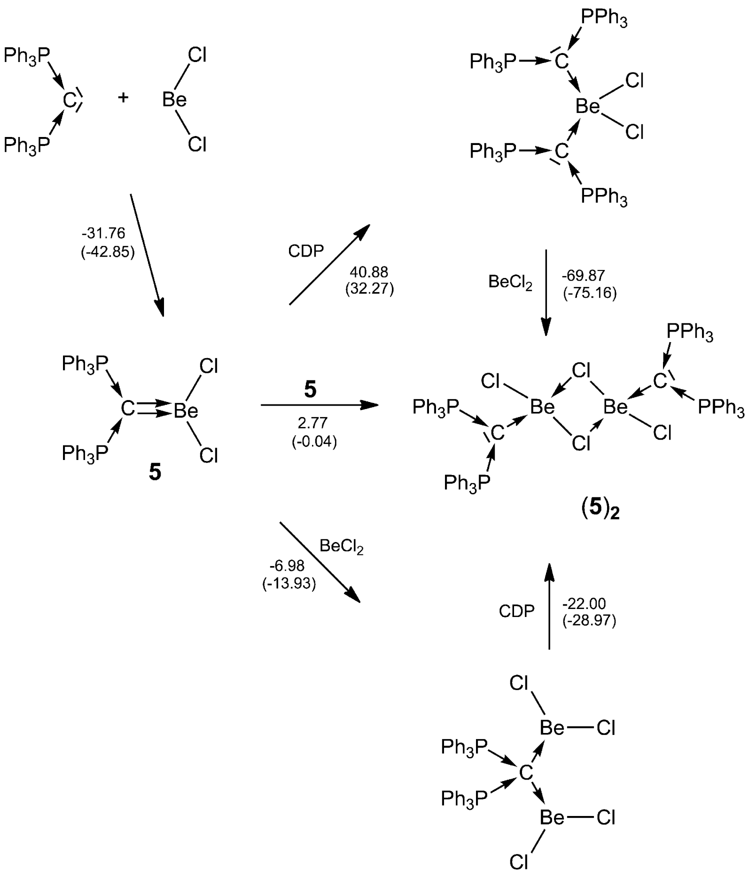
weaker than in the latter. The calculated BDE for loss of the second $\mathrm{BeCl_2}$ in the reaction $\mathrm{Cl_2Be}\leftarrow\mathbf{1}\rightarrow\mathrm{BeCl_2} \rightarrow \mathrm{Cl_2Be}\leftarrow\mathbf{1} + \mathrm{BeCl_2}$ is only D_e = 7.0 kcal·mol^{-1} which is much less than the BDE of **5**. Nevertheless, it seems possible that the "double-donor" complex $\mathrm{Cl_2Be}\leftarrow\mathbf{1}\rightarrow\mathrm{BeCl_2}$ might be formed as weakly bonded adduct with an excess of $\mathrm{BeCl_2}$.

Table 2. EDA results for $\mathrm{Cl_2Be}\leftarrow\mathbf{1}$ calculated with C_s symmetry. Energies in kcal·mol^{-1}.

Fragments	$\mathrm{BeCl_2}$ + **1**
ΔE_{int}	–62.4
$\Delta E_{\mathrm{Pauli}}$	96.7
$\Delta E_{\mathrm{elstat}}$ a)	–88.6 (55.7 %)
ΔE_{orb} a)	–70.5 (44.3 %)
a′ b)	–62.7 (89.0 %)
a′′ b)	–7.7 (11.0 %)

a) The percentage values in parentheses give the contribution to the total attractive interactions $\Delta E_{\mathrm{elstat}} + \Delta E_{\mathrm{orb}}$. b) The percentage values in parentheses give the contribution to the total orbital interactions ΔE_{orb}.

Two other donor-acceptor complexes of **1** and $\mathrm{BeCl_2}$ were investigated theoretically. One is the adduct $[\mathrm{BeCl_2\{C(PPh_3)_2\}_2}]$, where two carbodiphorphorane ligands bind to beryllium dichloride $\mathbf{1}\rightarrow\mathrm{BeCl_2}\leftarrow\mathbf{1}$. Complexes of $\mathrm{BeCl_2}$ with two ligands $\mathrm{BeCl_2L_2}$, where L is an oxygen or nitrogen donor ligand are well known.[30]. It is thus possible that $\mathbf{1}\rightarrow\mathrm{BeCl_2}\leftarrow\mathbf{1}$ could be formed when an excess of **1** is employed. Figure 3c shows the optimized geometry of the latter complex. The tetracoordinate beryllium atom of $\mathbf{1}\rightarrow\mathrm{BeCl_2}\leftarrow\mathbf{1}$ has much longer Be–C (1.965 Å and 2.020 Å) and Be–Cl (2.056 Å and 2.080 Å) bonds than in $\mathrm{Cl_2Be}\leftarrow\mathbf{1}$ (**5**) and $\mathrm{Cl_2Be}\leftarrow\mathbf{1}\rightarrow\mathrm{BeCl_2}$ (Table 1). The calculated energy for the dissociation reaction $\mathbf{1}\rightarrow\mathrm{BeCl_2}\leftarrow\mathbf{1} \rightarrow \mathrm{Cl_2Be}\leftarrow\mathbf{1} + \mathbf{1}$ indicates that the complex $\mathbf{1}\rightarrow\mathrm{BeCl_2}\leftarrow\mathbf{1}$ is only a local energy minimum structure, which is thermodynamically unstable toward loss of one ligand **1**. The fragments $\mathrm{Cl_2Be}\leftarrow\mathbf{1} + \mathbf{1}$ are 40.9 kcal·mol^{-1} lower in energy than the complex $\mathbf{1}\rightarrow\mathrm{BeCl_2}\leftarrow\mathbf{1}$. This is a dramatic difference to many dicoordinated complexes $\mathrm{L}\rightarrow\mathrm{BeCl_2}\leftarrow\mathrm{L}$ such as the adduct $\mathrm{(CH_2PPh_2)Ph_2P}\rightarrow\mathrm{BeCl_2}\leftarrow\mathrm{PPh_2(CH_2PPh_2)}$, which could become isolated and characterized by X-ray structure analysis.[23b] The latter complex has a calculated BDE for the second $\mathrm{PPh_2(CH_2PPh_2)}$ ligand of D_e = 16.8 kcal·mol^{-1} which should be compared with a negative BDE for the second $\mathrm{C(PPh_3)_2}$ ligand of $\mathbf{1}\rightarrow\mathrm{BeCl_2}\leftarrow\mathbf{1}$ (D_e = –40.9 kcal·mol^{-1}). The latter value also underscores the difference between the donor strength of carbenes and carbones. Theoretical studies have shown that $\mathrm{BeCl_2}$ may bind two nucleophilic carbenes such as $\mathrm{CF_2}$ in the complex $\mathrm{Cl_2Be(CF_2)_2}$ with nearly equal bond strength for the first (19.8 kcal·mol^{-1}) and second $\mathrm{CF_2}$ donor (18.6 kcal·mol^{-1}).[23a] This underlines the particular donor ability of a single ligand **1**.



Scheme 2. Schematic presentation of the relative energies /kcal•mol^{-1} at BP86/TZVPP//BP86/SVP of the complexes of $BeCl_2$ and **1**. The values in parentheses give the BDEs at BP86/SVP. For (**5**)$_2$ see also the tautomeric form of the Be_2Cl_2 ring. The double arrow in **5** represents the double lone-pair donation of the carbone donor; for details see text.

Scheme 2 shows an overview of the relative energies for the complexes of $BeCl_2$ and **1**. It shows also the energy for the formation of the chlorine bridged dimer (Cl_2Be←**1**)$_2$. The optimized geometry of the latter complex is shown in Figure 3d. The Be–Cl bonds of the moieties **5** are much longer in the dimer (2.033 Å and 2.050 Å) than in free **5**, whereas the Be–Cl bonds between the monomers (2.132 Å and 2.203 Å) are still longer. Scheme 2 shows that the formation of the dimer (Cl_2Be←**1**)$_2$ is slightly endoenergetic with respect to two monomers. It seems unlikely that (Cl_2Be←**1**)$_2$ is formed in the reaction of $BeCl_2$ with **1**.

4. Conclusion and Outlook

The use of 2-Br-fluorobenzene as the solvent in reactions with the carbodiphosphorane **1** instead of the usual solvents like toluene, THF, CH_2Cl_2, DMSO, or DME opens new aspects to the access of addition compound of the type **1**→*M* (*M* = transition metal or main group Lewis acids). 2-Br-fluorobenzene is polar enough to dissolve such adducts. Proton abstraction to give the favored cation [**1**→H]$^+$ is suppressed. The analysis of the bonding situation in Cl_2Be←**1** reveals that the orbital donation comes mainly from the σ lone-pair orbital of **1**, whereas the π donation is rather weak. However, the Cl_2Be←**1** π donation appears strong enough to make the donation of a second donor species **1** unfavorable. The calculation of **1**→Cl_2Be←**1** shows that the latter complex is higher in energy than **1**→Cl_2Be and free **1**. The carbodiphosphorane may bind, albeit weakly, a second $BeCl_2$ species in the complex Cl_2Be←**1**→$BeCl_2$. The bond dissociation energies for the first and second $BeCl_2$ fragments are D_e = 31.8 kcal•mol^{-1} and 7.0 kcal•mol^{-1}. The dimerization of Cl_2Be←**1** is energetically slightly endoenergetic.

5. Experimental Section

All operations were carried out in 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 with 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;[31] $BeCl_2$ was prepared from the elements.[30a] The solvent 2-bromofluorobenzene was dried with P_2O_5.

Preparation of [$Cl_2BeC\{PPh_3\}_2$] (5): A mixture of **1** (0.18 g, 0.34 mmol) and $BeCl_2$ (0.066 g, 0.55 mmol) in 2-Br-fluorobenzene (2 mL) was treated in an ultrasonic bath for 5 min followed by heating for 1 min. A tan colored solution with some insoluble material on top of the solution was obtained. The mixture was filtered and the solution layered with *n*-pentane (0.5 mL). Colorless crystals of **5** formed after

Table 3. Crystallographic data of the compounds $[Cl_2Be(C\{PPh_3\}_2)]$ (**5**), $(Ph_3PMe)Cl\cdot0.25$toluene (**6**), and $(H_2C\{PPh_3\}_2)Cl_2\cdot$DME (**8**).

	5	**6**	**8**
Formula	$C_{37}H_{30}BeCl_2P_2$	$C_{20.75}H_{20}ClP$	$C_{41}H_{42}Cl_2O_2P_2$
Mw /g·mol^{-1}	616.46	335.79	699.59
a /Å	10.076(1)	12.236(1)	12.999(1)
b /Å	10.883(1)	16.300(1)	19.720(1)
c /Å	15.211(2)	18.563(1)	14.634(1)
α /°	79.22(1)	90	90
β /°	84.76(1)	102.24(1)	106.09(1)
γ /°	69.90(1)	90	90
Crystal size /mm	$0.12 \times 0.11 \times 0.10$	$0.23 \times 0.08 \times 0.06$	$0.58 \times 0.08 \times 0.06$
Volume /Å^3	1538.1(3)	3618.2(4)	3604.3(4)
Z	2	8	4
d_{calc} /g·cm^{-3}	1.331	1.233	1.289
Crystal system	triclinic	monoclinic	monoclinic
Space group	$P\bar{1}$ (Nr. 2)	$P2_1/c$ (Nr. 14)	$P2_1/n$ (Nr. 14)
Diffractometer	IPDS II (Stoe)	IPDS II (Stoe)	IPDS II (Stoe)
Radiation	Mo-K_α	Mo-K_α	Mo-K_α
Temperature /K	100	100	100
μ /cm^{-1}	3.14	2.96	3.04
$2\theta_{max}$ °	51.92	51.92	51.84
Index range	$-12 \le h \le 12$ $-13 \le k \le 13$ $-17 \le l \le 18$	$-15 \le h \le 14$ $-20 \le k \le 20$ $-22 \le l \le 22$	$-14 \le h \le 15$ $-24 \le k \le 24$ $-17 \le l \le 17$
Number of rflns collected	11584	48136	25116
Number of indep. rflns (R_{int})	5888 (0.1168)	7033 (0.2269)	6981 (0.1053)
Number of observed rflns with $F_o > 4\sigma(F_o)$	2479	2440	4641
Parameters	380	427	508
Absorption correction	numerical	numerical	numerical
Structure solution	direct methods SIR-92[32]	direct methods SIR-92[32]	direct methods SIR-92[32]
Refinement against F^2	SHELXL-97[33]	SHELXL-97[33]	SHELXL-97[33]
Hydrogen atoms	calculated positions with common displacement parameter	calculated positions with common displacement parameter	calculated positions with common displacement parameter. H(1) and H(2) were refined free
R_1	0.0567	0.0409	0.0492
wR_2 (all data)	0.1208	0.0608	0.1167
max. electron density left / e·Å^{-3}	0.715	0.195	0.469

several days in high yields. **^{31}P NMR** (in 2-Br-fluorobenzene): 19.00 ppm. **IR** (Nujol mull): $\tilde{\nu}$ = 1587 w, 1479 s, 1437 s, 1261 w, 1235 w, 1111 vs. 1050 m, 1027 m, 997 m, 890 vs, 821 m, 751 s, 688 s, 654 m 546 m, 530 s, 523 s, 515 s, 497 s, 450 w, 417 w cm^{-1}. Although the ^{31}P NMR signals of **5** and of the cation $(HC\{PPh_3\}_2)^+$ are close together, a clear distinction by IR spectroscopy could be achieved.

Structure Determinations: Crystallographic data could be obtained for the compounds **5**, **6**, and **8**; crystals formed as described above. The molecular structure of **5** is shown in Figure 1 and Figure 2; crystallographic data are collected in Table 3. Compound **6** contains a molecule of toluene disordered around a center of symmetry. The DME molecule in **8** is disordered in two positions with occupation parameters 0.6 and 0.4. For structural details of $(Ph_3PMe)Cl\cdot0.25$toluene (**6**), and $(H_2C\{PPh_3\}_2)Cl_2\cdot$DME (**8**) see Supporting Information.

Crystallographic data (excluding structure factors) for the structures in this paper have been deposited with the Cambridge Crystallographic Data Centre, CCDC, 12 Union Road, Cambridge CB21EZ, UK. Copies of the data can be obtained free of charge on quoting the depository numbers CCDC-833915 (**5**), CCDC-833914 (**6**), and CCDC-833913 (**8**) (Fax: +44-1223-336-033; E-Mail: deposit@ccdc.cam.ac.uk, http://www.ccdc.cam.ac.uk).

Quantum Chemical Calculations: Geometry optimizations were carried out using the TurboMole optimizer[34] and gradients at the BP86[35]/def2-SVP[36] level of theory. The resolution-of-identity method was applied.[37] Stationary points were characterized as minima by calculating the Hessian matrix analytically at this level of theory. Additional single-point energy calculations at BP86 using the TZVPP basis set[36] were also performed.

For the bonding analysis of $Cl_2Be\leftarrow$**1** we optimized the molecule with the program package ADF2009.01.[38] BP86 was chosen applying uncontracted Slater-type orbitals (STOs) as basis functions.[39] The latter basis sets for all elements have triple-ζ quality augmented by two sets of polarization functions (ADF-basis set TZ2P). This level of theory is denoted BP86/TZ2P. An auxiliary set of s, p, d, f, and g STOs was used to fit the molecular densities and to represent the Coulomb and exchange potentials accurately in each SCF cycle.[40] Scalar relativistic effects were incorporated by applying the zeroth-order regular approximation (ZORA) in all ADF calculations.[41]

The interatomic interactions were investigated by means of an energy decomposition analysis (EDA) developed independently by *Morokuma*[42] and by *Ziegler* and *Rauk*.[43] The bonding analysis focuses on the instantaneous interaction energy ΔE_{int} of a bond A–B between two fragments A and B in the particular electronic reference state and in the frozen geometry of AB. This interaction energy is divided into three main components [Equation (3)].

$$\Delta E_{\mathrm{int}} = \Delta E_{\mathrm{elstat}} + \Delta E_{\mathrm{Pauli}} + \Delta E_{\mathrm{orb}} \quad (3)$$

The term $\Delta E_{\mathrm{elstat}}$ corresponds to the quasiclassical electrostatic interaction between the unperturbed charge distributions of the prepared atoms and is usually attractive. The Pauli repulsion $\Delta E_{\mathrm{Pauli}}$ is the energy change associated with the transformation from the superposition of the unperturbed electron densities $\rho_A + \rho_B$ of the isolated fragments to the wave function $\Psi^0 = N\hat{A}[\Psi_A\Psi_B]$, which properly obeys the Pauli principle through explicit antisymmetrization ($\hat{A}$ operator) and renormalization (N = constant) of the product wave function. $\Delta E_{\mathrm{Pauli}}$ comprises the destabilizing interactions between electrons of the same spin on either fragment. The orbital interaction ΔE_{orb} accounts for charge transfer and polarization effects. The ΔE_{orb} term can be decomposed into contributions from each irreducible representation of the point group of the interacting system. Since the molecules in our study have at least C_s symmetry, it is possible to estimate the intrinsic strength of orbital interactions from orbitals having a′ (σ) and a′′ (π) symmetry quantitatively. This directly gives the contributions of the σ and π orbital interactions to the ΔE_{orb} term:

$$\Delta E_{\mathrm{orb}}\ (C_s) = \Delta E_{\sigma}(a') + \Delta E_{\pi}(a'') \quad (4)$$

Further details on the EDA method[38] and its application to the analysis of the chemical bond[44] can be found in the literature.

Supporting Information: (see footnote on the first page of this article). Additional structural views and information on compounds **6** and **8** are given. We also give tables with the total energies and the coordinates of the calculated molecules.

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