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Carbenes as Pure Donor Ligands: Theoretical Study of Beryllium−Carbene Complexes[1]

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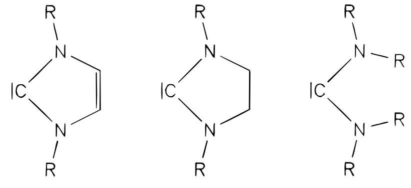
Quantum chemical ab initio calculations at the MP2/6-31G(d) level of theory are reported for the beryllium−carbene complexes $Be(CX_2)_n^{2+}$ (X = H, F; $n = 1-4$), $ClBe(CX_2)_n^{+}$ (X = H, F; $n = 1-3$), and $Cl_2Be(CX_2)_n$ (X = H, F; $n = 1, 2$). The complex $ClBe(C(NH_2)_2)_3^{+}$ has also been calculated. Where feasible, the bond energies of some molecules are reported at MP4/6-311G(d)//MP2/6-31G(d). Analysis of the bonding situation with the help of the natural bond orbital method shows that the carbene ligands are pure donors in the complexes. The dications $Be(CX_2)_n^{2+}$ (X = H, F; $n = 1-4$) have strong $Be^{2+}-C$ donor−acceptor bonds. The bond strengths decrease clearly when the number of ligands increases from $n = 1$ to 4. The CH_2 complexes have stronger Be−C bonds than the CF_2 complexes. Yet, the CH_2 complexes are chemically less stable than the CF_2 complexes for kinetic reasons. The carbon p(π) orbital of methylene stays nearly empty in the complexes, which makes them prone to nucleophilic attack. *All theoretical evidence indicates that the dominant factor which determines the chemical stability of carbenes and carbene complexes is the population of the carbon* p(π) *orbital.* The chemical instability of the methylene complexes becomes obvious by the geometry optimizations of $ClBe(CH_2)_2^{+}$, $ClBe(CH_2)_3^{+}$, $Cl_2Be(CH_2)$, and $Cl_2Be(CH_2)_2$, which lead to rearranged structures as energy minimum forms. The C−H bonds and particularly the C−F bonds of the ligands are shorter than in free CH_2 and CF_2. The carbon atom of CF_2 becomes electronically stabilized in the complexes via p(π) donation from fluorine. This finding suggests that carbene ligands, which are unstable as free molecules, may become sufficiently stabilized to be isolated even in complexes without metal → carbene back-donation.

1. Introduction

Carbene chemistry has been considerably boosted in recent years since Arduengo reported about the isolation of a series of imidazol-2-ylidenes **A** (Chart 1).[2] The scope of stable carbenes was later extended from the unsaturated species **A** to the related saturated imidazolin-2-ylidenes **B**, which for R = mesityl melts without decomposition at 107−109 °C.[3] The most recent development in this field was reported by Alder et al., who succeeded in crystallizing the first noncyclic carbene, i.e. bis(diisopropylamino)carbene **C**.[4] The dogma that carbenes are only transient species has disappeared, and synthetic organic chemistry has gained a new and exciting field of research.

The unexpected stability of the carbenes **A**−**C** prompted several groups to carry out theoretical studies in order to analyze the bonding situation of the unusual species.[5−9] After some controversy about the role of π-delocalization and possibly aromaticity in **A**, and a discussion about the importance of electronic and steric effects in stable carbenes, there is general agreement now that the dominant factor in stabilizing the carbenes **A**−**C** is the donation from the nitrogen lone pairs into the formally empty p(π) orbital of the carbene carbon atom.[8,9] Additional steric protection from the N-substituents may enhance the stability of the carbenes, and it may compensate for less electronic stabilization, but it is not the decisive factor. All theoretical and experimental evidence indicates that, in order to form a stable

Chart 1. Long-Lived Carbenes Isolated So Far



A B C

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carbene, the carbene carbon atom needs to be bonded to strong p(π) donor atoms.

Carbenes have been known as ligands in stable transition-metal donor−acceptor complexes since the epochal work of Fischer.[10] In the classical Fischer-type complexes the carbene ligands are bonded via donation from the carbon lone pair to an empty d(σ) orbital of the metal and via back-donation from an occupied d(π) orbital of the metal to the formally empty p(π) orbital of carbon. The analysis of metal−carbene bonding has shown that $R_2C \rightarrow ML_n$ donation and $R_2C \leftarrow ML_n$ back-donation are significant.[11] A different bonding situation may exist in donor−acceptor complexes of stable carbenes, because of the unusual electronic structures of the species. In contrast to the classical carbene complexes, the carbenes **A**−**C** appear to be pure donor ligands, and a number of carbene complexes with transition metals as well as main-group elements have been reported.[2a,12−15] In particular the main-group metal−carbene complexes appear as a rather new field in synthetic organometallic chemistry. Since carbenes **A**−**C** need no π-back-donation from the metal into the p(π) orbital of carbon in order to become isolable, a number of stable adducts with main-group elements, which usually do not form stable donor−acceptor complexes with carbenes, have been synthesized. We were particularly intrigued by the report that beryllium, which cannot back-donate p(π) electrons, forms stable complexes with carbene ligands **A**.[14b] In previous theoretical studies we had predicted that beryllium should be capable of forming very stable donor−acceptor complexes with various donors and that even a stable adduct between BeO and He with a bond energy $D_e = \sim 3$ kcal/mol should exist.[16] Several of the theoretically predicted BeO complexes have recently been observed experimentally,[17] but the reported species are only stable in inert matrices, due to the strong tendency of BeO to polymerize. The report by Herrmann et al.[14b] that nucleophilic carbenes **A** with R = CH_3 can split the polymeric structure of beryllium chloride to form a tris(carbene) complex $[ClBe(\mathbf{A})_3]^+[Cl]^-$ may lead to yet another new field of exciting chemistry.

We report the first theoretical analysis of the bonding situation in beryllium carbene complexes. In order to understand the electronic structure of the molecules, we carried out ab initio calculations of the series of model compounds $Be(CX_2)_n{}^{2+}$ (X = H, F; n = 1−4), $ClBe(CX_2)_n{}^+$ (X = H, F; n = 1−3), and $Cl_2Be(CX_2)_n$ (X = H, F; n = 1, 2). CH_2 in the $^1A_1$ state, which has an empty p(π) orbital at carbon, has been chosen as a reference carbene. CF_2 was chosen as model for a π-donor stabilized carbene, because it has a partly filled p(π) AO at carbon and electronegative substituents. The complex $ClBe(C(NH_2)_2)_3{}^+$ was included in this study for a comparison with the recently synthesized $ClBe(\mathbf{A})_3{}^+$, where **A** = 1,3-dimethylimidazol-2-ylidene.[14b] We were interested in the electronic structures and the different bonding properties of the XCH_2 and XCF_2 complexes. To this end we calculated the equilibrium geometries and metal−carbene bond energies of the compounds. The bonding situation was analyzed with the natural bond orbital (NBO) method developed by Weinhold.[18] The interpretation of the nature of donor−acceptor bonding using the NBO method and a comparison with the results of other methods has been given before.[18]

2. Methods

The geometries of the molecules have been fully optimized at the Hartree−Fock (HF) and MP2 (Møller−Plesset perturbation theory terminated at second order)[19] levels of theory using a 6-31G(d) basis set.[20] In each case several conformations with different symmetry have been used as starting geometries, and additional geometry optimizations were carried out without symmetry constraints. The nature of the stationary points was investigated by calculating the Hessian matrices and the vibrational frequencies at HF/6-31G(d) and MP2/6-31G(d). All structures shown here are minima on the potential energy surface (number of imaginary frequencies $i = 0$). Improved energies have been obtained for some molecules at MP4(SDTQ) using a 6-311G(d) basis set.[21] The ZPE (zero-point vibrational energy) corrections were calculated from the harmonic frequencies; all ZPE values are unscaled. Unless otherwise noted, results are discussed at the highest level of theory employed for the respective molecule, i.e. MP4(SDTQ)/6-311G(d)//MP2/6-31G(d) or MP2/6-31G(d)//MP2/6-31G(d). The calculations have been carried out using the program packages Gaussian 92 and Gaussian 94.[22]

3. Results and Discussion

Figure 1 shows the optimized geometries of the beryllium carbene complexes **1**−**15** and the donor and

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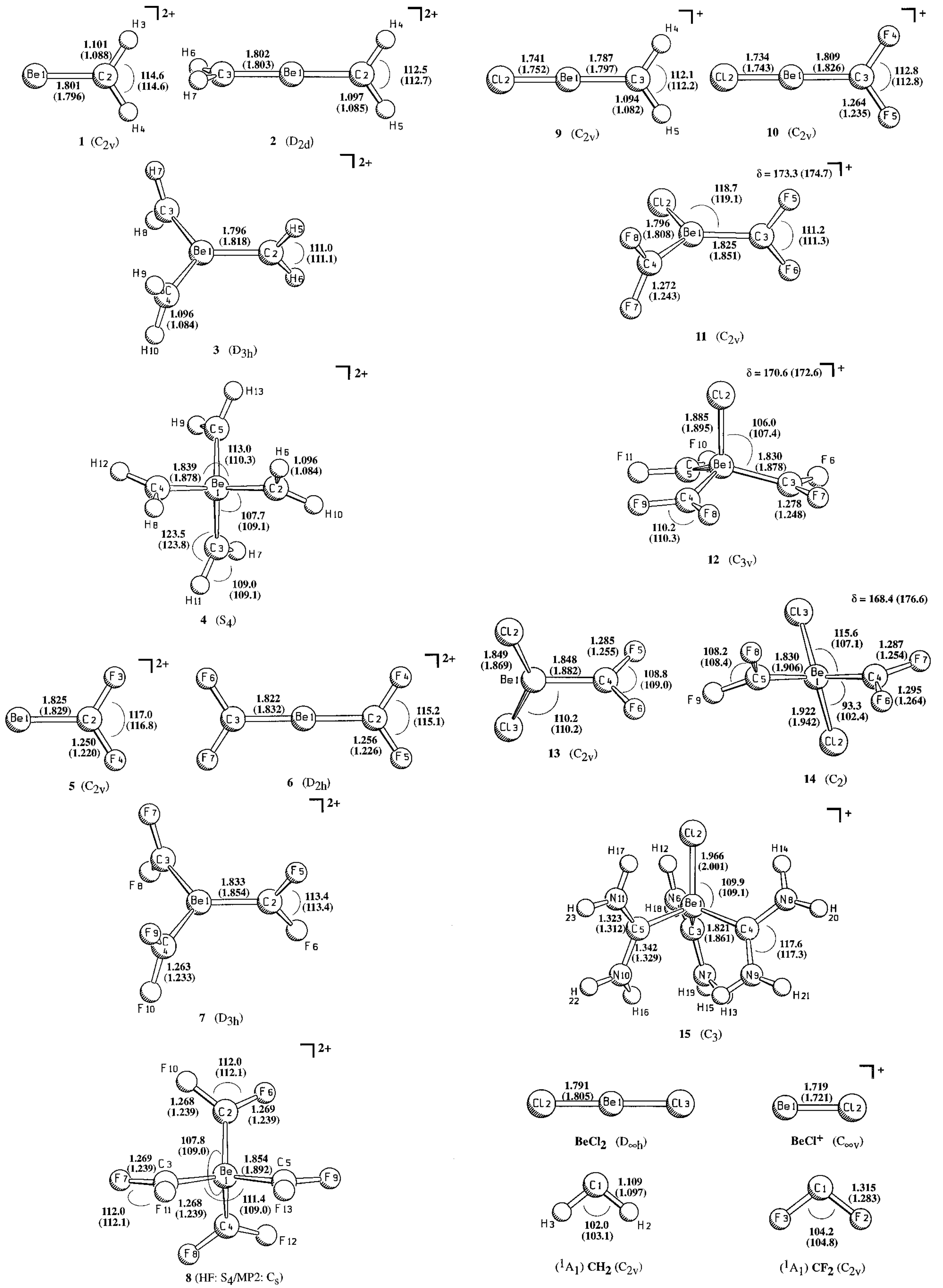
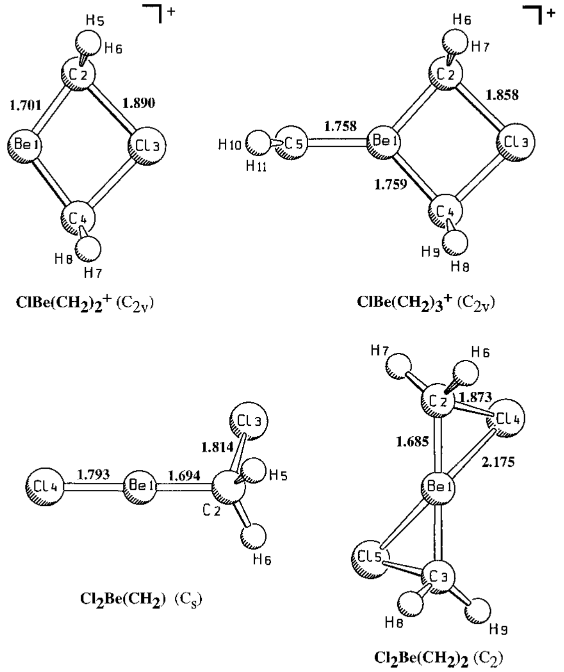


Figure 1. Optimized geometries at MP2/6-31G(d) of **1**–**15**. Distances are given in Å and angles in deg. The angle δ is the bond angle Be–C–X, where X is a dummy atom lying in the CF_2 plane along the Be–C axis. Values at HF/6-31G(d) are given in parentheses.

acceptor fragments. The geometry optimizations of the CH_2 complexes $ClBe(CH_2)_n^+$ ($n = 2, 3$) and $Cl_2Be(CH_2)_n$ ($n = 1, 2$) did not lead to carbene complexes as energy minimum structures. The calculations gave bridged or other rearranged forms which are shown in Figure 2. Table 1 gives the calculated energies of the carbene



$ClBe(CH_2)_2^+$ (C_{2v})

$ClBe(CH_2)_3^+$ (C_{2v})

$Cl_2Be(CH_2)$ (C_s)

$Cl_2Be(CH_2)_2$ (C_2)

Figure 2. Results of the geometry optimizations of $ClBe(CH_2)_2^+$, $ClBe(CH_2)_3^+$, $Cl_2Be(CH_2)$, and $Cl_2Be(CH_2)_2$. The structures shown are minima on the potential energy surfaces ($i = 0$) but may be not the global energy minima.

complexes **1**−**15** and the donor and acceptor fragments. The bond energies calculated at the correlated levels are not very different from the Hartree−Fock values. This indicates that the theoretically predicted bond energies should be quite reliable. The results of the NBO analysis are listed in Table 2.

The calculated beryllium−carbon distances of the doubly charged mono-, di-, and tricarbene complexes $Be(CH_2)_n^{2+}$ (**1**−**3**) have about the same value ~1.80 Å (Figure 1), which is ~0.1 Å longer than a typical Be−C single bond. For comparison: the calculated Be−C bond length of $Be(CH_3)_2$ is 1.693 Å (MP2/6-31G(d)).[23] The Be−C distance of the tetracarbene **4** is somewhat longer (1.839 Å). The optimized structure of $Be(CH_2)_2^{2+}$ (**2**) has orthogonal CH_2 groups (D_{2d} symmetry), while the CF_2 groups of $Be(CF_2)_2^{2+}$ (**6**) are in the molecular plane (D_{2h} symmetry). In both cases, the rotational barrier about the Be−C bond is very low, however (<0.1 kcal/mol). The very weak hyperconjugation in **2** and the very weak π-donation in **6** are the reasons for the perpendicular and planar arrangements of the CX_2 groups, respectively. A more detailed discussion of the differences between the CH_2 and CF_2 complexes is given below.

The beryllium−carbon bond lengths of the fluorocarbene complexes $Be(CF_2)_n^{2+}$ (**5**−**8**) are 0.02−0.03 Å longer than those of **1**−**4**. The calculated metal−carbene bond energies of the CF_2 complexes are also lower than the bond energies of the respective CH_2 complexes (Table 1). The Be^{2+}−CX_2 bonds are rather strong; the calculated values are D_e = 167.7 kcal/mol for **1** and D_e = 132.8 kcal/mol for **5**. The bond energies decrease significantly when the number of carbene ligands increases. The fourth CX_2 ligand in **4** is bonded with D_e = 59.3 kcal/mol, and the value for **8** is D_e = 54.8 kcal/mol, which are, however, still rather strong donor−acceptor bonds. Structure **4** is a rare example for a molecule with S_4 symmetry. The corresponding CF_2 complex **8** has C_s symmetry at the MP2/6-31G(d) level (S_4 at HF/6-31G(d); see Figure 1), but the potential energy surface for the distortion from S_4 to C_s is very flat.

The results of the NBO analysis for **1**−**8** indicate that the beryllium atom carries most of the positive charge of the dications (Table 2). It is noteworthy that the partial charge at Be in the CH_2 complexes is nearly the same as in the respective CF_2 complexes. As a result of the complex formation, there is a significant change in the partial charges of the CH_2 and CF_2 ligands. The NBO results suggest that the flow of electronic charge from the CX_2 ligands to Be^{2+} comes from hydrogen and fluorine, respectively, while the carbon atom even gains electronic charge in the course of complex formation. The carbon atoms in **1**−**4** are more negative than in free CH_2, and the carbon atoms in **5**−**8** are less positive than in CF_2 (Table 2). The Be−C bond formation between the carbon lone pair and Be^{2+} is accompanied by a charge flow from carbon to beryllium, which makes the carbon atom more electronegative. However, the resulting electron flow from H or F toward C overcompensates the electron flow from C to Be^{2+}. This is in agreement with the calculated shortening of the C-H and particularly C−F bonds in the complexes **1**−**8** relative to free CH_2 and CF_2. We want to point out that the carbon p(π) orbital of CF_2 has a much higher occupancy in the complexes than in free CF_2 (Table 2). The additional p(π) charge cannot come from back-donation from the metal, because beryllium has no p electrons. This is an important result, because it means that carbenes, which are not stable as free species, may still be found as ligands in stable carbene complexes without that back-donation from the metal to the carbene takes place.

The NBO analysis yields true bond orbitals for the donor−acceptor bonds between Be and C of **1**−**13** and **15**, while pure carbon lone pair orbitals are found for **14**. The bond orbitals are strongly polarized toward the carbon end, rather than carbon lone pair orbitals. The polarization toward carbon is always >85% (Table 2). The hybridization of the Be−C bond orbitals of **1**−**8** changes significantly with increasing number of carbene ligands. The % s character at the carbon (beryllium) end increases (decreases), and the polarization toward carbon becomes stronger from the mono- to the tetracarbenes. This means that the C → Be donor orbitals become more tightly bonded at carbon, which is in accord with the decrease of the bond energies from **1** to **4** and from **5** to **8**. The fact that the Be^{2+}−CF_2 bonds are weaker in comparison to the respective Be^{2+}−CH_2 bonds can be explained by the hybridization of the carbon lone pair in CH_2 and CF_2. The electron pair at the carbon end of the CF_2 complexes has a higher % s character than that of the CH_2 complexes (Table 2) as predicted by Bent's rule.[24] It is also lower in energy because of the electronegative fluorine substituents. Both factors make CF_2 a poorer electron donor than CH_2.

Only the first member of the series $ClBe(CH_2)_n^+$ (n = 1−3) has a carbene complex as energy minimum structure, i.e. $ClBe(CH_2)^+$ (**9**). The geometry optimizations of $ClBe(CH_2)_2^+$ and $ClBe(CH_2)_3^+$ lead to bridged struc-

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Table 1. Calculated Total Energies E_{tot} (au), Zero-Point Vibrational Energies ZPE (kcal/mol), Dissociation Energies of One Carbene CX_2 D_e (kcal/mol), and ZPE Corrected Values D_0 (kcal/mol)

		HF/6-31G(d)//HF/6-31G(d)		MP2/6-31G(d)//MP2/6-31G(d)			MP4/6-311G(d)//MP2/6-31G(d)	
molecule	no.	E_{tot}	D_e	E_{tot}	ZPE	D_e (D_0)	E_{tot}	D_e (D_0)
$Be(CH_2)^{2+}$	**1**	−52.754 00	170.6	−52.855 42	16.9	172.9 (166.9)	−52.924 33	167.7 (161.6)
$Be(CH_2)_2{}^{2+}$	**2**	−91.841 67	135.1	−92.045 53	30.4	138.1 (135.4)	−92.169 56	134.1 (131.4)
$Be(CH_2)_3{}^{2+}$	**3**	−130.854 69	88.3	−131.167 42	46.3	95.3 (90.3)	−131.347 29	91.8 (86.8)
$Be(CH_2)_4{}^{2+}$	**4**	−169.812 80	53.8	−170.234 49	60.4	60.9 (57.6)	−170.473 33	59.3 (56.1)
$Be(CF_2)^{2+}$	**5**	−250.473 50	127.4	−250.936 11	9.9	134.8 (129.4)	−251.172 18	132.8 (127.4)
$Be(CF_2)_2{}^{2+}$	**6**	−487.297 69	102.6	−488.220 82	14.9	108.6 (108.1)	−488.677 75	107.1 (106.5)
$Be(CF_2)_3{}^{2+}$	**7**	−724.064 22	66.4	−725.449 17	22.0	73.3 (70.7)	nc[a]	
$Be(CF_2)_4{}^{2+}$	**8**	−960.799 46	46.7	−962.648 71	28.7	55.2 (53.0)	nc[a]	
$ClBe(CH_2)^{+}$	**9**	−512.873 81	104.5	−513.126 83	16.8	106.3 (101.9)	−513.301 52	106.4 (102.0)
$ClBe(CF_2)^{+}$	**10**	−710.613 79	74.2	−711.224 19	9.2	78.6 (75.3)	−711.564 77	81.2 (78.0)
$ClBe(CF_2)_2{}^{+}$	**11**	−947.340 09	41.1	−948.407 93	15.8	45.3 (43.20	nc[a]	
$ClBe(CF_2)_3{}^{+}$	**12**	−1184.046 87	28.9	−1185.576 44	22.5	35.7 (33.5)	nc[a]	
$Cl_2Be(CF_2)$	**13**	−1170.449 59	16.4	−1171.198 64	9.6	19.8 (17.6)	−1171.641 01	17.9 (15.8)
$Cl_2Be(CF_2)_2$	**14**	−1407.130 22	12.5	−1408.339 80	16.2	18.6 (16.4)	nc[a]	
$ClBe(C(NH_2)_2)_3{}^{+}$	**15**	−921.360 70		−922.864 20	nc[a]		nc[a]	
CH_2 ($^1A_1$)		−38.872 37		−38.970 07	10.8		−39.031 48	
CF_2 ($^1A_1$)		−236.660 74		−237.111 57	4.5		−237.334 89	
$BeCl_2$		−933.762 64		−934.055 55	3.0		−934.277 55	
$BeCl^{+}$		−473.834 84		−473.987 38	1.5		−474.100 45	
Be^{2+}		−13.609 80		−13.609 80	0.0		−13.625 60	

[a] Not calculated.

Table 2. Results of the NBO Analysis at MP2/6-31G(d): Bond Order P(AB), p(π) Population of Be and C, Partial Charges q, Polarization and Hybridization of the Be−C Donor−Acceptor Bond

	P			p(π)		q				Be−C					
molecule	Be−C	C−F/ H/N	Be−Cl	Be	C	Be	C	F/H/ NH_2	Cl	% Be	% C	% s(Be)	% p(Be)	% s(C)	% p(C)
1	0.42	0.88		0.00	0.01	1.74	−0.33	0.30		12.6	87.4	81.7	17.8	26.6	73.2
2	0.41	0.90		0.00	0.01	1.44	−0.26	0.27		11.5	88.5	49.8	50.0	32.1	67.9
3	0.30	0.91		0.01	0.04	1.39	−0.29	0.25		7.6	92.4	33.3	65.9	35.3	64.6
4[a]	0.24	0.91[b]			0.05	1.35	−0.28	0.22[b]		5.4	94.7	26.2	72.4	37.9	62.0
5	0.36	1.15		0.00	0.52	1.76	0.55	−0.15		11.0	89.0	81.5	17.8	34.7	65.2
6	0.37	1.13		0.00	0.50	1.46	0.62	−0.17		10.7	89.3	49.7	50.0	40.1	59.9
7	0.29	1.10		0.01	0.49	1.37	0.61	−0.20		7.4	92.6	33.3	65.2	43.1	56.9
8[a]	0.23[b]	1.07[b]			0.47[b]	1.31	0.61[b]	−0.22[b]		5.5[b]	94.5[b]	26.2[b]	71.6[b]	44.9[b]	55.1[b]
9	0.36	0.91	0.60	0.07	0.02	1.38	−0.25	0.23	−0.59	9.7	90.3	54.7	45.1	35.5	66.5
10	0.32	1.09	0.62	0.07	0.47	1.38	0.63	−0.21	−0.58	8.9	91.0	54.9	44.7	42.1	57.8
11	0.26	1.06	0.45	0.06		1.34	0.62	−0.24	−0.63	6.2	93.8	35.6	61.7	45.4	54.6
12[a]	0.22	1.03	0.31			1.30	0.61	−0.25	−0.61	5.0	95.0	29.1	67.9	47.7	52.3
13	0.19	1.01	0.38	0.06	0.44	1.36	0.62	−0.28	−0.71	4.5	95.5	35.5	59.8	47.5	52.5
14	0.18	0.98	0.29			1.35	0.58	−0.30	−0.68	0.0	100.0			63.3	36.7
		1.00						−0.28							
15	0.18	1.31[b]	0.26			1.43	−0.01	0.06[b]	−0.74	4.1	95.9	26.7	72.2	33.7	66.3
CH_2 ($^1A_1$)		0.96			0.01		−0.17	0.08							
CF_2 ($^1A_1$)		0.94			0.34		0.71	−0.36							
$BeCl_2$			0.48	0.07		1.38			−0.69						
$BeCl^{+}$			0.67	0.09		1.59			−0.59						

[a] Three-center bonds encountered in the NBO analysis. [b] Averaged over almost identical values for symmetry-inequivalent atoms, bonds, or groups.

tures, where chlorine forms two bonds with two methylene groups, as minima on the potential energy surface (Figure 2). The driving force for the formation of the bridged structures is the electrophilic character of the CH_2 groups. For $ClBe(CH_2)_3{}^{+}$ we found another higher lying energy minimum structure where the chlorine atom bridges all three CH_2 groups. Since we are concerned with the structures and energies of carbene complexes, we did not explore other energy minimum forms of the compounds, and we do not discuss the structures shown in Figure 2. Unlike the methylene complexes, energy minimum structures of the whole series of difluorocarbene complexes $ClBe(CF_2)_n{}^{+}$ with $n = 1-3$ were found. This result confirms the conclusion that the chemical stability of carbenes and carbene complexes is crucially influenced by π-donation from the ligand atoms.

Figure 1 shows the theoretically predicted geometries of $ClBe(CH_2)^{+}$ (**9**) and $ClBe(CF_2)_n{}^{+}$ ($n = 1-3$; **10**−**12**). The CF_2 ligands of **11** and **12** are slightly pyramidal (δ = 173.3 and 170.6°, respectively). The Be−Cl bonds of the complexes are significantly longer than in free $BeCl^{+}$ (1.719 Å). It is interesting to note that the Be−Cl bond length of $ClBe(CF_2)_n{}^{+}$ increases considerably with the number of carbene ligands, from 1.734 Å in **10** to 1.796 Å in **11** and 1.889 Å in **12** (Figure 1). Yet, the calculated Be−Cl bond length of **12** is still much shorter than the experimental value for the carbene complex $ClBe(\mathbf{A})_3{}^{+}$ (2.076 and 2.091 Å), although the experimental values for the Be−C bond length of $ClBe(\mathbf{A})_3{}^{+}$ (1.807 and 1.822 Å for two independent molecules in the unit cell) are in reasonable accord with the calculated Be−C distance of **12** (1.830 Å).[14b] In order to see if the difference in the Be−Cl bond lengths may be due to the different carbene ligands, we optimized the geometry of the aminocarbene complex **15**. Figure 1 shows that **15** has a shorter Be−C bond length (1.821 Å) than **12** (1.830 Å). This is reasonable, because diaminocarbene is a better donor (higher lying HOMO) than CF_2. The calculated Be−C bond length of **15** is in good agreement with the experimental values of $ClBe(\mathbf{A})_3^+$.[14b] Noticeable is the significantly longer Be−Cl bond of **15** (1.966 Å) as compared to that of **12** (1.889 Å). Although the calculated Be−Cl bond of **15** is still shorter than the experimentally reported Be−Cl bond of $ClBe(\mathbf{A})_3^+$, the difference might partially be due to the better donor ability of 1,3-dimethylimidazol-2-ylidene compared to diaminocarbene. It seems that the donor strength of the carbene donor **A** has a strong influence upon the Cl−Be bond length of $ClBe(\mathbf{A})_3^+$.

The beryllium−carbene bond strength of the cations **9**−**12** is clearly lower compared with the respective dications (Table 1). This result is not surprising, since Be^{2+} should be a stronger acceptor than $ClBe^+$. The $ClBe-(CH_2)^+$ bond strength is $D_e = 106.4$ kcal/mol. The bond strength in the series $ClBe(CF_2)_n^+$ decreases from $D_e = 81.2$ kcal/mol ($n = 1$, **10**), to $D_e = 45.3$ kcal/mol (n = 2, **11**), and finally to $D_e = 35.7$ kcal/mol ($n = 3$, **12**). Note that the Be−C bond length of $ClBe(CH_2)^+$ (**9**) is *shorter* than in $BeCH_2^{2+}$ (**1**), as it is *shorter* in $ClBe-CF_2^+$ (**10**) than in $BeCF_2^{2+}$ (**5**) (Figure 1), although the bond strength is *higher* in the doubly charged cations. This can be explained by the nature of the Be−C donor−acceptor bonds in the molecules. The donor lone pairs of CH_2 and CF_2 in $ClBeCH_2^+$ (**9**) and $ClBeCF_2^+$ (**10**) have a higher % s character than in $BeCH_2^{2+}$ (**1**) and $BeCF_2^{2+}$ (**5**), respectively (Table 2). This makes the donor lone pairs of **9** and **10** more compact and more tightly bonded to the carbon atom, which leads to shorter Be−C distances and lower dissociation energies.

Neutral carbene complexes of $BeCl_2$ could only be found with CF_2 as ligand but not with CH_2. Geometry optimization of Cl_2BeCH_2 and $Cl_2Be(CH_2)_2$ gave the rearranged structures shown in Figure 2 as energy minimum forms. The optimized geometries of Cl_2BeCF_2 (**13**) and $Cl_2Be(CF_2)_2$ (**14**) are shown in Figure 1. The Be−C distances are still rather short (1.848 Å for **13** and 1.830 Å for **14**). The ligand dissociation energies of the neutral complexes are nearly the same for the monocarbene **13** ($D_e = 19.8$ kcal/mol) and the dicarbene **14** ($D_e = 18.6$ kcal/mol, Table 1), which are clearly lower than the bond energies of the cations. Noteworthy are the long Be−Cl bond lengths of **13** (1.849 Å) and particularly **14** (1.922 Å). The very long Be−Cl bond of **14** makes it plausible that the reaction of beryllium chloride with the carbene **A** gave the ionic compound $ClBe(\mathbf{A})_3^+$ rather than $Cl_2Be(\mathbf{A})_2$, although this may be formed as an intermediate.

The NBO analysis suggests that the Be−C donor−acceptor bonds (carbene lone pairs) of the neutral complexes **13** and **14** are least polarized toward beryllium among the calculated compounds (Table 2), which is in agreement with chemical intuition. Complex **14** is the only molecule for which the NBO analysis gives pure carbon lone pair orbitals rather than polarized Be−C bond orbitals. A comparison of the NBO results between $ClBe(CF_2)_2^+$ (**11**) and $Cl_2Be(CF_2)_2$ (**14**) shows nicely that the Be−C bonding in the complexes cannot be understood on the basis of electrostatic interactions between the Lewis base CF_2 and the Lewis acids $BeCl^+$ and $BeCl_2$, respectively. The partial charges at beryllium and carbon are very similar in the two compounds, but the Be−C bond energy of **14** ($D_e = 18.6$ kcal/mol) is less than half of the Be−C bond energy of **11** ($D_e = 45.3$ kcal/mol). We also want to point out that the NBO analysis supports the assignment of **1**−**14** as pure donor-complexes without metal → carbene back-donation. Table 2 shows that the p(π) occupation at Be in the complexes is virtually the same as in the acceptor fragments.

It is instructive to compare the structures and energies of the neutral and charged CH_2 and CF_2 complexes **1**−**14**. The calculated results show clearly that the CH_2 complexes have stronger donor−acceptor bonds than the CF_2 complexes. This is also found for transition metal−carbene complexes $M(CO)_5CH_2$ and $M(CO)_5CF_2$ (M = Cr, Mo, W), which have calculated bond energies $D_o = 84.2-90.8$ kcal/mol for the $M-CH_2$ bonds, and $D_o = 38.6-47.5$ kcal/mol for the M-CF_2 bonds.[25] It means that CH_2 is a stronger Lewis base than CF_2 in complexes with and without metal → C back-donation. The chemical instability of carbenes and carbene complexes where the carbene C atom is not stabilized by π-donor ligands must be due to the unoccupied p(π) orbital, which makes the carbene prone to nucleophilic attack. The CF_2 complexes are kinetically more stable than the CH_2 complexes, although CH_2 forms stronger Be−carbene bonds than CF_2. The highly electrophilic character of the CH_2 group becomes also obvious by the calculated results of the beryllium carbene complexes. For example, the rotational barriers about the Be−C bonds in **3** are 3.4 kcal/mol for rotation of one CH_2 group and 10.5 kcal/mol for rotation of all three CH_2 groups. This is in contrast to the rotation of the CH_2 groups in **2**, which has virtually no barrier. The reason for the hindered rotation in **3** is the hyperconjugative donation of the Be−C bond orbital into the empty p(π) orbital of the adjacent carbene C atom. In case of $ClBe(CH_2)_2^+$, $ClBe(CH_2)_3^+$, $Cl_2Be(CH_2)$, and $Cl_2Be(CH_2)_2$, the hyperconjugative donation from the chlorine lone pairs leads even to different types of structures as energy minimum forms. This demonstrates the strongly electron deficient character of the CH_2 groups.

Table 2 shows that the carbon p(π) orbital of **3** has a small electron population, which is in agreement with the noticeable rotational barrier. The corresponding CF_2 complex **7** has a much lower rotational barrier than **3** (0.4 kcal/mol for one CF_2 group, 0.9 kcal/mol for all three CF_2 groups), because the carbon p(π) orbital is populated by donation from the fluorine lone pairs (Table 2). The lower rotational barriers of **7** compared with **3** show clearly that steric interactions are not the reason for the hindered rotation of the CH_2 groups of **3**. The optimized geometries show that the CF_2 groups in **11**−**14** are always arranged in such a way that the p(π) orbital of the carbon atoms and the Be−Cl bonds are parallel. This indicates a stabilizing interaction between the Be−Cl bond and the partially occupied carbon p(π) orbital. One explanation could be a weak hyperconjugative interaction between the occupied Be−Cl orbital and the still partially empty carbon p(π) orbital. This would also explain the small tilt (pyramidalization)

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[25] Ehlers, A. W.; Dapprich, S.; Vyboishchikov, S. F.; Frenking, G. *Organometallics* **1996**, *15*, 105.

of the CF_2 ligands toward the Be−Cl bonds, which enhances the overlap between the Be−Cl orbital and the carbon p(π) orbital. The reversed interaction, i.e. *negative* hyperconjugation between the partially occupied carbon p(π) orbital and the Be−Cl antibonding σ^* orbital can be excluded, because the population of the Be p(π) orbital in **6** is zero (Table 2). Another explanation for the geometries of **11**−**14** could be dipole−dipole interactions between the strongly polarized Be−Cl bond and the carbon lone pair.

This study makes clear that *the key for the isolation of carbenes and carbene complexes is the amount of electron donation into the empty p(π) orbital of the carbene carbon atom*, which is necessary to protect the carbene from nucleophilic attack. This can be achieved (i) by coordination of an unstable carbene to a transition metal that is able to back-donate sufficient electronic charge, (ii) by π-donating substituents at the carbene C-atom like in the stable amino-substituted carbenes **A**−**C**, but also (iii) by coordinating a π-donor substituted carbene to a pure acceptor metal, which leads to enhanced π-donation from the substituents to the carbene as in case of the beryllium carbenes.

Summary and Conclusion

The beryllium−carbene complexes **1**−**14** show significant differences between the carbon p(π) unsaturated CH_2 species and the π-donor stabilized CF_2 compounds. The Be^{2+}−C donor−acceptor bonds of $Be(CH_2)_n^{2+}$ are clearly stronger compared with the respective bonds in $Be(CF_2)_n^{2+}$. The bond strengths of the Be−C bonds decrease strongly when the number of carbene ligands increases. However, the methylene complexes are chemically less stable than the CF_2 complexes, because the carbon p(π) orbital of CH_2 stays nearly unoccupied in the complexes. This makes the CH_2 complexes prone to nucleophilic attack. The population of the carbon p(π) orbital is the dominating factor for the stability of the carbene complex. The chemical instability of the methylene complexes becomes obvious by the geometry optimizations of $ClBe(CH_2)_2^+$, $ClBe(CH_2)_3^+$, $Cl_2Be(CH_2)$, and $Cl_2Be(CH_2)_2$, which lead to bridged structures as energy minimum forms. The beryllium−carbon donor−acceptor bonds of the cations $ClBe(CH_2)^+$ and $ClBe(CF_2)_n^+$ are weaker than those of the dications, but the bonds are still quite strong. An important result has been found for the carbon atom of the CF_2 ligand. The formation of the complex leads to enhanced p(π) donation from fluorine to carbon, which yields a shorter C−F bond and an increase of the p(π) occupancy at carbon. This means that carbenes, which are unstable as free molecules, may be found in stable complexes without metal → carbene back-donation taking place. The Be−Cl bonds of $ClBe(CF_2)_n^+$ and $Cl_2Be(CF_2)_n$ are clearly longer than in $BeCl_2$. A particularly long Be−Cl bond has been calculated for $ClBe(C(NH_2)_2)_3^+$, which is in agreement with the very long Be−Cl bond found by X-ray structure analysis of $ClBe(\mathbf{A})_3^+$.

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