The Molecular Structures of Cyclopentadienylberyllium Bromide, (C₅H₅)BeBr, and Cyclopentadienylberyllium Acetylide, (C₅H₅)BeCCH, Determined by Gas Phase Electron Diffraction

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$(C_5H_5)BeBr$ and $(C_5H_5)BeCCH$ have been studied by gas phase electron diffraction. Both compounds contain symmetrically π-bonded (C_5H_5) rings. The bond distances and estimated standard deviations are: $(C_5H_5)BeBr$: $C-C=1.424(2)$ Å, $Be-C=1.950(12)$ Å, $Be-Br=1.943(15)$ Å. $(C_5H_5)BeCCH$: $C-C=1.428(2)$ Å, $Be-C(Cp)=1.919(5)$ Å, $Be-C\equiv=1.634(8)$ Å, $C\equiv C=1.231(10)$ Å.

The investigations of CpBeBr (Cp = cyclopentadienyl) and CpBeCCH by means of gas phase electron diffraction reported here are part of a series of investigations of compounds of the type CpBeX. Similar studies of Cp_2Be,[1] $CpBeCH_3$,[2] $CpBeCl$,[3] and $CpBeBH_4$[4] have already been published.

EXPERIMENTAL AND CALCULATION PROCEDURE

CpBeBr was supplied by Drew and Morgan,[5] CpBeCCH by Starowieyski and Morgan.[6]

Both were used without further purification. The electron scattering pattern was recorded on Balzers Eldiograph KD-G2. The experimental conditions are summarized in Table 1. The data were processed and the molecular structure refined using the program packages described by Andersen et al.[7] and Seip et al.[8]

Theoretical intensity curves were calculated from:

$$I^{AC}(s) = \sum_{i \neq j} \frac{|f_i(s)||f_j(s)|}{|f_A(s)||f_C(s)|} \cos[\eta_i(s) - \eta_j(s)] \frac{\sin(R_{ij}s)}{R_{ij}}$$
$$\exp(-\tfrac{1}{2}l^2_{ij}s^2)$$

The sum extends over all atom pairs i, j in the molecule. R_{ij} is the internuclear distance, l_{ij} the root mean square amplitude of vibration. $f_j(s) = |f_j(s)|\exp[i\eta_j(s)]$ is the complex atomic scattering factor of atom j.

The molecular structure was refined by least-squares calculations on the intensity data with a non-diagonal weight matrix and a separately refined scale factor for the intensity data obtained for each nozzle-to-plate distance. The

Table 1. Information about the intensity data.

Compound	$(C_5H_5)BeBr$		$(C_5H_5)BeCCH$	
Nozzle to plate distance (mm)	498.86	249.04	498.58	248.80
Nozzle temperature	50 − 55°	50 − 55°	80 − 85°	80 − 85°
Number of plates used	5	4	3	4
Atom A eqn. (1)	Br	Br	C	C
s-Range (Å⁻¹)	1.500 − 14.750	3.500 − 30.000	1.500 − 15.250	2.500 − 28.500
Increment (Å⁻¹)	0.125	0.250	0.125	0.250

standard deviations obtained were expanded to take into account an estimated uncertainty of 0.1 % in the electron wavelength.

Radial distribution functions were calculated by Fourier inversion of experimental and theoretical intensity curves after multiplication with the artificial damping function $\exp(-ks^2)$. The experimental intensity functions were then first spliced to each other and then to the theoretical curve calculated for the best model below $s = 1.50$ Å^{-1}.

STRUCTURE REFINEMENT

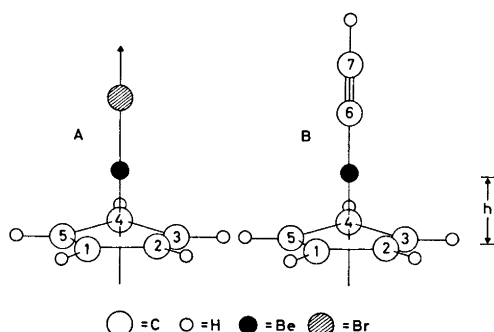It was assumed that both compounds contain symmetrically π-bonded Cp rings, as do CpBeCl and CpBeMe. Molecular models are shown in Fig. 1. It was further assumed that both molecules have C_{5v} symmetry. Since H-atoms could not be located with great precision it was assumed that the Cp rings are completely planar. Bastiansen-Morino shrinkage effects were neglected for both molecules.

CpBeBr. The molecular structure is determined by four independent parameters, *e.g.* by the C – H, C – C, Be – C, and Be – Br bond distances. These were refined along with the

Fig. 1. Molecular models of $(C_5H_5)BeBr$ (A) and $(C_5H_5)BeCCH$ (B).

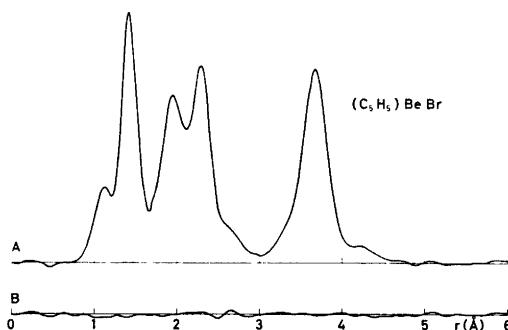*Fig. 2.* A: Experimental radial distribution curve for $(C_5H_5)BeBr$. Artificial damping constant $k = 0.0025$ Å^2. B: Difference between the experimental curve and a theoretical curve calculated for best model.

Table 2. Interatomic distances (r_a) and root mean square vibrational amplitudes (l) of $(C_5H_5)BeBr$ and $(C_5H_5)BeCCH$. (Estimated standard deviations in parentheses). For numbering of the C atoms consult Fig. 1. The H atoms are numbered as the C atoms to which they are bonded.

	$(C_5H_5)BeBr$ r_a (Å)	l (Å)	$(C_5H_5)BeCCH$ r_a (Å)	l (Å)
Bond distances				
$C_1 - H_1$	1.087(7)	0.044(12)	1.127(8)	0.060(12)
$C_1 - C_2$	1.424(2)	0.034(4)	1.428(2)	0.038(3)
$Be - C_1$	1.950(12)	0.110(23)	1.919(5)	0.085(4)
$Be - Br$	1.943(15)	0.02(6)		
$Be - C_6$			1.634(8)	0.091(23)
$C_6 - C_7$			1.231(10)	0.058(12)
$C_7 - H_7$			1.060^a	0.060(12)^b
h	1.528(16)		1.487(5)	
Non-bonded distances				
$C_1 \cdots C_3$	2.303(3)	0.053(4)	2.310(3)	0.062(6)
$C_1 \cdots H_2$	2.242(6)	0.096(25)	2.280(7)	0.050(16)
$C_1 \cdots H_3$	3.353(7)	0.088(14)	3.400(7)	0.096(23)
$Br \cdots C_1$	3.676(4)	0.097(3)		
$Br \cdots H_1$	4.162(5)	0.255(30)		
$C_1 \cdots C_6$			3.349(7)	0.103(9)
$C_1 \cdots C_7$			4.518(7)	0.146(7)
$Be \cdots C_7$			2.865(8)	0.041(19)

^{a} Assumed value. ^{b} $l(C_1 - H_1)$ and $l(C_7 - H_7)$ were assumed equal.

nine most important vibrational amplitudes. The resulting values and their estimated standard deviations are listed in Table 2. The generalized R-factor [8]

$$R_3 = 100(\sum_k \sum_l P_{kl} V_k V_l / \sum_k \sum_l P_{kl} I_k I_l)$$

was equal to 14.8. The two amplitudes l (Be − C) and l(Be − Br) are strongly correlated, the correlation coefficient being $\varrho = -0.91$. As a consequence these amplitudes are poorly determined. The $C_1 - C_2$ vibrational amplitude obtained in this compound as well as in CpBeCCH is very low. This is probably due to an error in the blackness correction that was employed. However, parallel refinement on benzene data strongly indicates that the effect of the error is confined to the values obtained for the smallest vibrational amplitudes, i.e. $l(C_1 - C_2)$ and $l(C_1 - H_1)$.

CpBeCCH. The molecular structure is determined by six parameters, e.g. by the bond distances $C_1 - H_1$, $C_1 - C_2$, Be − C_1, Be − C_6, $C_6 - C_7$, and $C_7 - H_7$. The latter was fixed at 1.06 Å and not refined. The remaining five bond distances were refined along with the twelve most important vibrational amplitudes. The resulting values and their estimated standard deviations are listed in Table 2. The generalized R-factor was $R_3 = 14.4$.
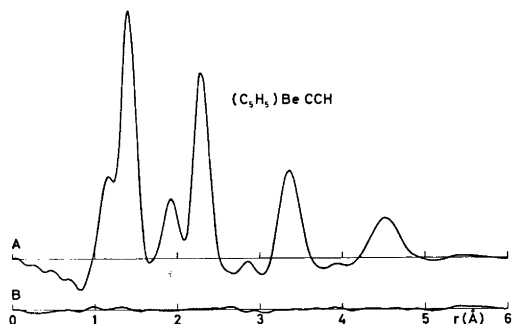

Fig. 3. A: Experimental radial distribution curve for (C_5H_5)BeCCH. Artificial damping constant $k = 0.0025$ Å². B: Difference between the experimental curve and a theoretical curve calculated for the best model.

DISCUSSION

No significant differences are found between the CpBe fragments in the two molecules studied here or those previously described.[1-4]

While the Be-C(methyl) bond distance in CpBeCH₃ is equal to the Be-C bond distance in free monomeric $(CH_3)_2$Be [9] the Be − Cl bond distance in CpBeCl was found to be about 0.08 Å longer than in free monomeric BeCl₂.[10] It was suggested that the bonds in BeCl₂ are shortened by dative π-bonding and that such π-bonding is absent − or at least reduced − in CpBeCl because the pertinent Be $2p$ atomic orbitals are used for bonding to the Cp ring via the $e_1\pi$-orbitals of the latter. This view receives some support from recent MO-calculations on Cp₂Be,[11] which show that bonding between Be and the nearest Cp ring is effected primarily through molecular orbitals formed from the ring $e_1\pi$-orbitals and the $2p_x$ and $2p_y$ atomic orbitals on Be.

The Be − Br distance found in CpBeBr is greater than in free monomeric BeBr₂,[10] 1.92 ± 0.02 Å, but not significantly so. Because of greater disparity in the size of the pertinent p orbitals in BeBr₂ than in BeCl₂ one would perhaps expect less dative π-bonding in the former compound.

The Be − C≡ bond distance in CpBeCCH is considerably shorter than the terminal Be − C≡ bond distance in dimeric methylpropynylberyllium-trimethylamine,[12] 1.75 Å. The latter bond length must, however, have been increased considerably through formation of the dative N→Be bond, as can be seen from the fact that the Be − C bond distance in $(CH_3)_2$Be,[5] 1.70 Å is increased to 1.83 Å in dimethylbis(quinuclidine)beryllium.[13]

The Be − C_6 bond in CpBeCCH is also considerably shorter than the Be − C(methyl) bond in CpBeCH₃, but the difference is of the order expected on going from sp^3- to sp-hybridized C. The $C_6 - C_7$ triple bond distance is not significantly different from the triple bonds in $H_3C = C \equiv CH_3$ [14] or $HC \equiv C - C \equiv CH$.[15]

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