BERYLLIUM

ANNUAL SURVEY COVERING THE YEARS 1975 AND 1976

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With only slight exaggeration, one can say that more effort has been expended on calculations on organoberyllium species than on their preparation and chemistry.

Calculations have been reported on the following compounds, real and hypothetical:

- Dimethylberyllium (ab initio calculations) (1). The calculated Be-C distance (1.701Å) agreed well with the known bond distance in Me_2Be monomer (1.698Å). The calculations indicated that there is no π bonding and that there is free rotation about the Be-C bond.
- Methylberyllium fluoride monomer (single configuration SCF wave functions) (2). The Be-C and Be-F bond distances, the dipole moment and the quadrupole moment were calculated.
- The molecules CH_3BeH, $CH_2(BeH)_2$, $CH(BeH)_3$ and $C(BeH)_4$ (RHF/STO-3G calculations) (3). These calculations relate to the tetrahedral vs. planar carbon atom problem. A steady decrease in the planar-tetrahedral energy differences was noted on going from CH_3BeH to $C(BeH)_4$.
- Neutral Be and Be^+ complexes of ethylene and acetylene, as a catalysis-related model of the interaction of metal atoms and unsaturated hydrocarbons (4). As might be expected, the interaction of Be^+ (ground ^2S state) with both substrates was calculated to be attractive. The nature of the interaction of neutral Be with ethylene (attractive or repulsive) depended on the electronic state of the Be atoms. Back-

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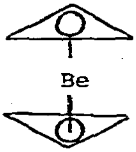
Beryllium, Annual Survey covering the year 1974 see J. Organometal. Chem., 98(1975)117-123.

bonding from the unsaturated ligand to Be was found to be important and the general agreement with the Dewar/Chatt-Duncanson model for transition metal-olefin complexes was noted.

- Sandwich-type organoberyllium compounds, including the known dicyclopentadienylberyllium, as well as several exotic, unknown species, such as compounds 1-4 (5). An explanation



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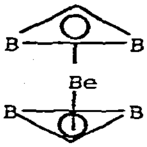

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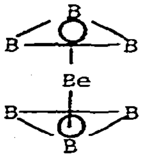

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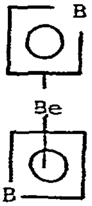
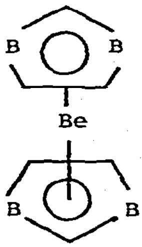


4

for the strange distorted structures of $(C_5H_5)_2Be$ in the gas phase and in the solid state was given in terms of the MO's involved, rather than in terms of the usually cited steric factors. Similar calculations showed bis(η^3-cyclopropenyl)-beryllium to be less stable that the η^1,η^1-bonded alternative. The authors speculate that the following sandwich molecules may be more stable than the η^1 alternatives in the gas phase:



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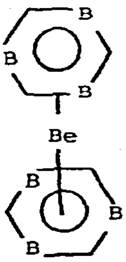

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$H_{11}B_{10}C\text{-}Be\text{-}CB_{10}H_{11}$

7

Another author has explained the distorted structure of dicyclopentadienylberyllium (and of analogous Sn(II) and Pb(II) compounds) on the basis of Jahn-Teller effects (6).

Experimental studies on cyclopentadienylberyllium compounds also have been reported. NMR spectra of dicyclopentadienylberyllium, taken between -50° and -135° in CF_2Cl_2 solution, showed only a single sharp peak with a half-width of 2.5 Hz in this temperature range (7). Conclusions about the solution structure of this compound were not possible. The microwave spectra of C_5H_5BeH, C_5H_5BeD, $^{13}CC_4H_5BeH$ and $^{13}CC_4H_5BeD$ have been measured by Haaland and his coworkers (8). A symmetrical top structure (Figure 1) was found, with d(Be-H) = 1.32Å and d(C-C) = 1.423Å and a dipole moment of 2.08D. German workers have reported the ^{13}C NMR spectra of C_5H_5BeBr and C_5H_5BePh (9). In the case of the former, $^{13}C-^{9}Be$ coupling (J = 1.1 Hz) was observed. The IR and Raman spectra of liquid and solid cyclopentadienylberyllium chloride, borohydride and borodeuteride were studied by Coe et al. (10). Vibrational assignments of most of the C_5H_5, BeX and skeletal modes were recorded. Cyclopentadienylberyllium borohydride was determined to have a double hydrogen bridge configuration as shown in 8. This structure persists from the gas phase to the liquid to the solid phase (in contrast to what has been reported

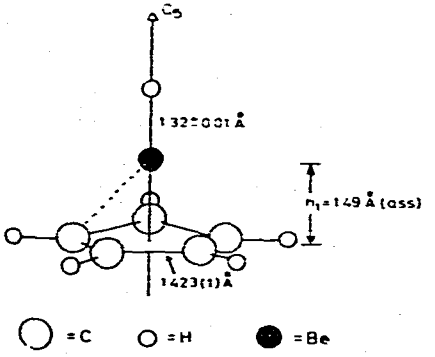
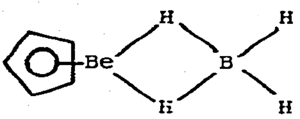


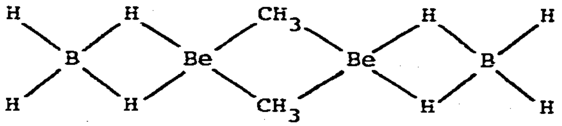
FIGURE 1. Molecular Model of Cyclopentadienylberyllium Hydride. From Bartke, Bjørseth, Haaland, Marstokk and Møllendal, J. Organometal. Chem., 85 (1975) 271



(8)

for Be(BH$_4$)$_2$). Internal rotation about the symmetry axis in $C_5H_5BeBH_4$ is hindered, with a torsional barrier of 500 cm^{-1}. Also to be noted is a Ph.D. thesis devoted to cyclopentadienylberyllium compounds (11).

French workers have prepared complexes of di-tert-butylberyllium with trimethyl- and triethylamine and -phosphine and studied their IR and Raman spectra at -180° (12). The results of this and of a previous study on other $(Me_3C)_2Be$-Lewis base complexes (with ethers and sulfides) were discussed in another paper (13). Di-tert-butylberyllium is a good "basicity indicator" toward hard bases on the basis of the appropriately evaluated spectroscopic data. The vibrational spectra of methylberyllium borohydride, which was found by means of vapor density measurements to be dimeric in the gas phase, have been studied in the gas phase and in the solid state (14). The solid also is made up of dimeric units, with the BH_4 group attached to the beryllium atom <u>via</u> a double hydride bridge, as in the case of $C_5H_5BeBH_4$. The Raman spectra of CH_3BeBH_4 and solid $(CH_3)_2Be$ were compared; it was concluded that $(CH_3BeBH_4)_2$ contains two methyl bridges. Its structure thus would be that shown in <u>9</u>.



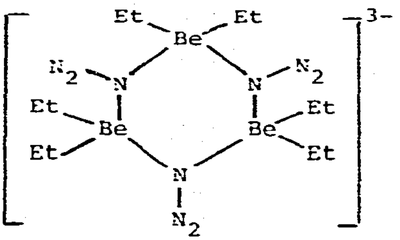
<u>9</u>

Atam and Dehnicke prepared organoberyllium azides (15):

$$2\ Et_2Be + Me_3SiN_3 \longrightarrow EtBeN_3BeEt_2$$

$$Et_2Be + CsN_3 \xrightarrow{\text{toluene}} Cs_3(Et_2BeN_3)_3$$

Both products are extremely sensitive to air and moisture, the anionic azido complex being pyrophoric in air. The structure of the anion, on the basis of its vibrational spectrum, was suggested to be 10, and that of the $Et_4Be_2N_3$ complex either 11 or 12. During the course of this study an improved preparation of ethylberyllium chloride by the redistribution reaction was developed (15):



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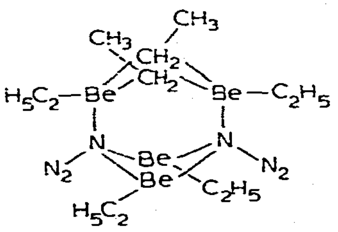

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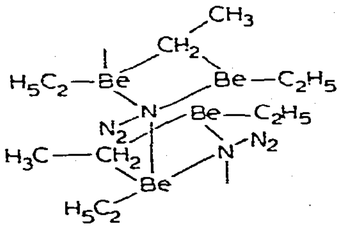

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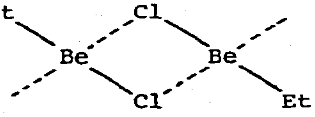
$$Et_2Be + BeCl_2 \longrightarrow 2\ EtBeCl$$

Its vibrational spectra indicated that chlorine, not ethyl, bridging gives an associated structure, 13.



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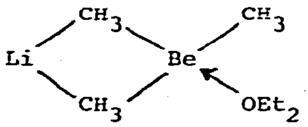
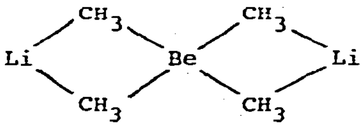
The system $nCH_3Li/(CH_3)_2Be$ in diethyl ether was examined by IR and proton NMR spectroscopy and the "ate" complexes 14, 15 and 16, believed to have the structures shown on the basis of the spectral data, were identified. When a 2:1



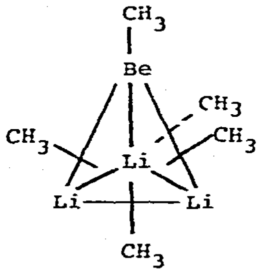
$LiBe(CH_3)_3 \cdot OEt_2$

14



$Li_2Be(CH_3)_4$

15



$Li_3Be(CH_3)_5$

16

$CH_3Li/(CH_3)_2Be$ mixture in ether was studied by NMR, all three complexes, 14, 15 and 16, were found to be present at equilibrium, with the following processes occurring to lead to this result:

$$1/4\ (CH_3Li)_4 + (CH_3)_2Be \longrightarrow LiBe(CH_3)_3$$

$$LiBe(CH_3)_3 + 1/4\ (CH_3Li)_4 \longrightarrow Li_2Be(CH_3)_4$$

$$Li_2Be(CH_3)_4 + 1/4\ (CH_3Li)_4 \longrightarrow Li_3Be(CH_3)_5$$

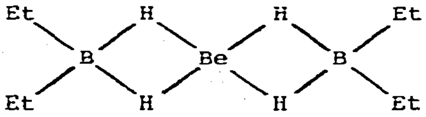
Hydrogenolysis of diethyl ether solutions containing CH_3Li and $(CH_3)_2Be$ in 1:1, 2:1 and 3:1 molar ratio using reaction with lithium aluminum hydride gave Li_2BeH_4 in the case of the 1:1 and 2:1 mixtures and Li_3BeH_5 with the 3:1 mixture. The reaction course shown below was suggested:

$$LiBe(CH_3)_3 + LiAlH_4 \longrightarrow Li_2Be(CH_3)_3H + AlH_3$$

$$Li_2Be(CH_3)_3H + AlH_3 \longrightarrow Li_2BeH_4 + Al(CH_3)_3$$

The reaction of $LiBe(CH_3)_3$ with AlH_3 provided $LiBeH_3$, while the 1:2 $CH_3Li/(CH_3)_2Be$ mixture, presumably containing $LiBe_2(CH_3)_5$, on reaction with $LiAlH_4$ gave a product of indefinite composition.

The compound $Be(Et_2BH_2)_2$, prepared by reaction of sym-tetraethyldiborane with diethylberyllium at 0° and presumably of structure 17, gave >71% pure beryllium hydride,

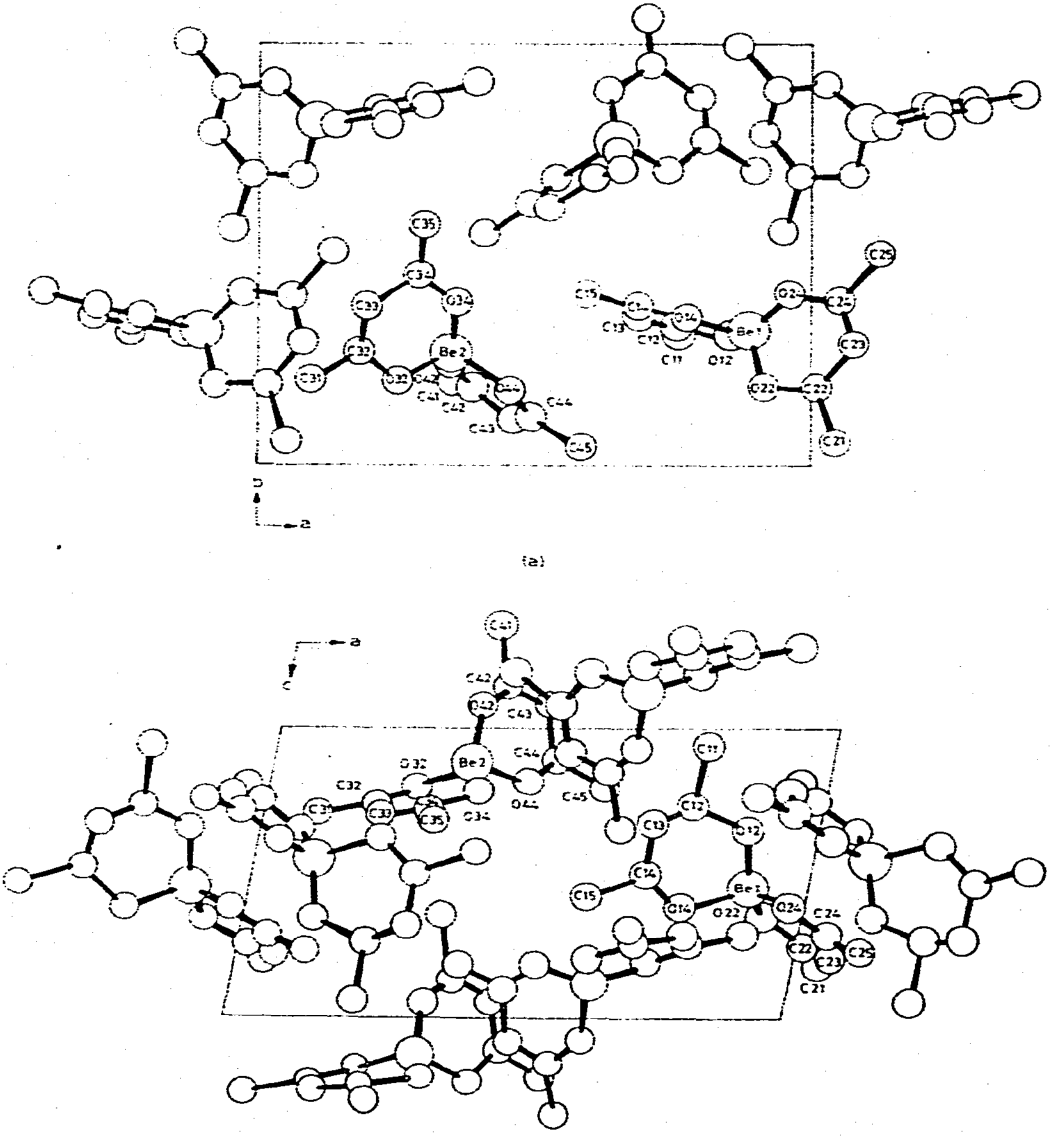


17

BeH_2, when heated at reduced pressure at 180° for 4-6 hr. (17). Treatment of dimethyl- and diethylberyllium with B_4H_{10} gave nonvolatile liquids of type $(Me_3B_3H_4)_2(BeH_2)_2(MeBeH)_2$, $B_3H_7(EtBeH)BeH_2BH_2$ and $B_3H_7(MeBeH)_4BH_2Me$ (18).

Finally, we mention three organic beryllium compounds without Be-C bonds which may be of interest to organometallic chemists.

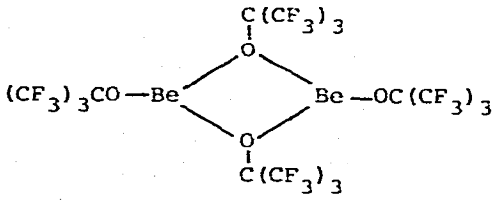
- Dimeric bis(nonafluoro-tert-butoxy)beryllium, 18, prepared by reaction of $(CF_3)_3COH$ with diethylberyllium (19). In contrast, the reaction of $(CF_3)_3CONa$ with beryllium chloride in diethyl ether gave $[(CF_3)_3CO]_2Be{\cdot}OEt_2$, which is monomeric in benzene. 2:1 Complexes, $[(CF_3)_3CO]_2Be{\cdot}2L$, were formed with L = ammonia and pyridine.



(a)

(b)

FIGURE 2. The Structure of Bis(2,4-pentanedionato)-beryllium. (a) Projection along the *c* axis; (b) Projection along the *b* axis. From J. M. Stewart and B. Morosin, Acta Cryst., B31 (1975) 1164.



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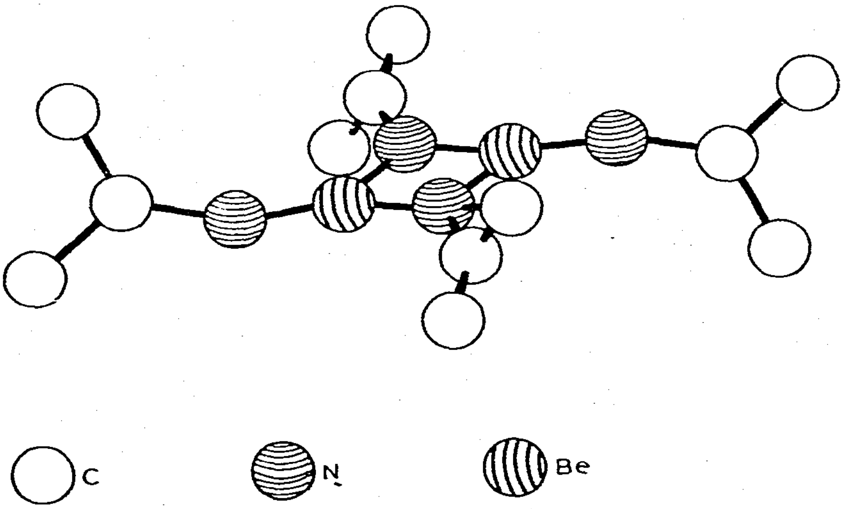
- Bis(2,4-pentanedionato)beryllium, $Be(CH_3COCHCOCH_3)_2$. An X-ray crystal structure determination confirmed that Be-O bonds are involved (Figure 2) (20).

- Dimeric bis(di-tert-butylmethyleneamino)beryllium, $\{Be[N=C(CMe_3)_2]_2\}_2$, prepared by reaction of diisopropylberyllium with $(Me_3C)_2C=NH$ in diethyl ether, was found in an X-ray diffraction study to have the structure shown in Figure 3 (21). The terminal methyleneamino ligands are seen to involve nonlinear C=N-Be units, but the observed bond distances and IR data indicated that $N \rightarrow B$ π-bonding is not significantly diminished by this deviation from linearity.



Skeleton of $[Be(N{:}CBu^t_2)_2]_2$. Interatomic distances (pm): Be—N_μ 168; Be—N_t 150; C=N_μ 128; C=N_t 127; Be. . .Be 223. Bond angles (°): Be—N_μ—Be' 83; N_μ—Be N_μ' 97; Be'. . .Be—N_t 161; Be—N_t=C 161; N_t—Be—N_μ 129; Be—N_μ=C 138.

FIGURE 3. Structure of the Bis(di-tert-butylmethyleneamino)-beryllium Dimer. From J. B. Farmer, H. M. M. Shearer, J. D. Sowerby and K. Wade, J. Chem. Soc., Chem. Comm. (1976) 160.

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