BERYLLIUM

ANNUAL SURVEY COVERING THE YEAR 1974

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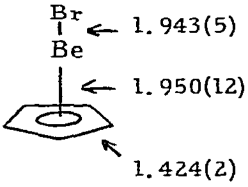
Activity in the area of organoberyllium chemistry continues on a very modest scale.

Gas phase electron diffraction studies by Haaland and Novak (1) have shown cyclopentadienylberyllium bromide and ethynylcyclopentadienylberyllium both to contain symmetrically π-bonded C_5H_5 rings. Bond distances in Å units are shown in 1 and 2. Attempts



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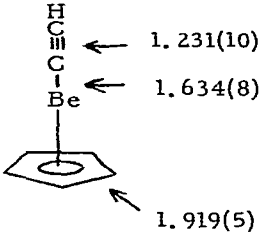

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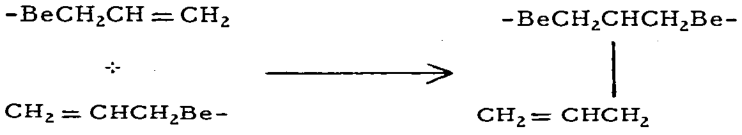
to prepare diallylberyllium by the exchange reaction between diethylberyllium and triallylborane have been reported (2). The exchange reaction did go to completion in the absence of solvents or in hydrocarbon medium, but the diallylberyllium formed underwent self-addition:

[+] Beryllium, Annual Survey covering the year 1973 see J. Organometal. Chem., 75(1975)1-4.



$$\begin{array}{l} \text{-BeCH}_2\text{CH}=\text{CH}_2 \\ \quad + \\ \text{CH}_2=\text{CHCH}_2\text{Be-} \end{array} \longrightarrow \begin{array}{l} \text{-BeCH}_2\text{CHCH}_2\text{Be-} \\ \qquad\quad | \\ \text{CH}_2=\text{CHCH}_2 \end{array}$$

as indicated by the virtual absence of propene and the presence of 4-methyl-1-pentene in substantial amounts when the solid product, which was pyrophoric in air, was hydrolyzed. The presence of a nonadiene also suggested the occurrence of some dehydroberyllation. In THF the diethylberyllium/triallylborane exchange was incomplete, but the allylberyllium which was formed only underwent partial self-addition.

Andersen and Coates have studied the reactions of beryllium alkyls with ketones and aldehydes and with imines (3). Addition to the C = O group, reduction and simple complex formation were observed, depending on the substituents on beryllium and on the C = O group:

$$Ph_2Be + Ph_2C=O \longrightarrow (PhBeOCPh_3)_2$$

$$(Me_3SiCH_2)_2Be + Ph_2C=O \longrightarrow (Me_3SiCH_2BeOCPh_2CH_2SiMe_3)_2$$

$$(Me_3C)_2Be + Ph_2C=O \longrightarrow (Me_3CBeOCHPh_2)_2$$

$$R_2Be + (Me_3C)_2C=O \longrightarrow (Me_3C)_2C=O \rightarrow BeR_2 \quad (R = Ph,\ Me_3SiCH_2)$$

$$Me_2Be + (Me_3C)_2C=O \longrightarrow (MeBeOCMe(CMe_3)_2)_2$$

$$2\ (Me_3C)_2Be + (Me_3C)_2C=O \longrightarrow (Me_3CCHO)_2Be$$

$$R_2Be + (Me_3C)_2C=O \longrightarrow (RBeOCH(CMe_3)_2)_2 \quad (R = Et,\ Me_3C)$$

$$Me_3CBeCl + (Me_3C)_2C=O \longrightarrow (ClBeOCH(CMe_3)_2)_2$$

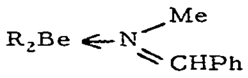
$$(Me_2CHCH_2)_2Be + Me_3CCH=O \longrightarrow (Me_2CHCH_2BeOCH_2CMe_3)_2$$

$$(Me_3C)_2Be + Me_3CCH{=}O \longrightarrow (Me_3CBeOCH(CMe_3)_2)_2$$

$$(Me_3C)_2Be{\cdot}OEt_2 + Me_2C{=}O \longrightarrow (Me_3CBeOCHMe_2)_2$$

With imines complex formation and C = N addition predominated:

$$R_2Be + PhCH{=}NMe \longrightarrow$$



$$R_2Be \leftarrow N(Me){=}CHPh \qquad (R = Me,\ Ph)$$

$$Me_2Be + PhCH{=}NAr \longrightarrow (MeBeN(Ar)CHMePh)_2$$

$$Et_2Be + PhCH{=}NR \longrightarrow (EtBeN(Me)CHEtR)_2 \qquad (R = Me,\ Ph)$$

A few examples of reduction were observed, e.g.:

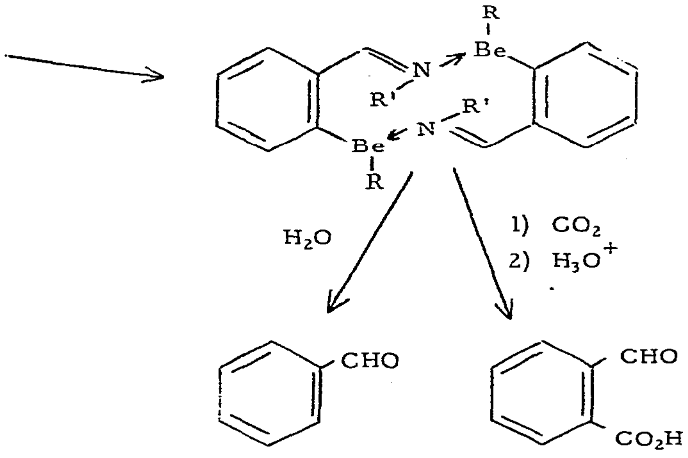
$$(Me_3C)_2Be + PhCH{=}NMe \longrightarrow (Me_3CBeN(Me)CH_2Ph)_2$$

Unexpected ortho-metalation also was encountered in a few cases:

$R_2Be + PhCH{=}NR'$

($R = Et,\ Me_3C$;

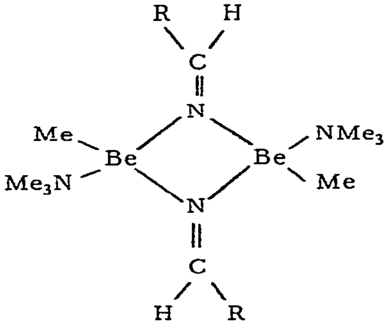
$R' = Me_3C$)



tert-Butyl cyanide formed 1:1 adducts with $(Me_3C)_2Be$ and Me_3CBeCl (3), but RC≡N compounds (R = Me_3C and Ar) underwent C = N addition reactions with methylberyllium hydride in triethylamine (4):

$$MeBeH + RC{\equiv}N \xrightarrow{Me_3N} (MeBeN{=}CHR \cdot NMe_3)_2 \quad (R = Me_3C,\ Ph,\ \underline{o}\text{-and } \underline{m}\text{-}CH_3C_6H_4)$$

The products have the following structure:



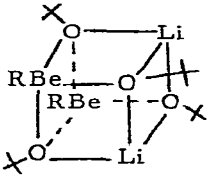
$$Me_3CBeH + Me_3CC{\equiv}N \xrightarrow{Me_3N} (Me_3CBeN{=}CHCMe_3 \cdot NMe_3)_2$$

U.S. patents describe the preparation of methylberyllium hydride by reaction of dimethylberyllium and beryllium hydride (5), the preparation of dimethylberyllium by reaction of $BeCl_2 \cdot 2Et_2O$ with $NaAlMe_4$ (6) and the purification and isolation of diisopropyl- and di-tert-butylberyllium by distillation (7).

A detailed study of alkali metal alkylberyllium alkoxides has been made by Andersen and Coates (8). Such compounds were prepared as follows:

$RLi + Be(OCMe_3)_2 \longrightarrow (LiRBe(OCMe_3)_2)_2$

The structure of this product was suggested to be 3.



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$Me_3CLi + Be(OCEt_3)_2 \longrightarrow (Li(CMe_3)Be(OCEt_3)_2)$

(monomer-dimer equilibrium)

$Me_3CLi + LiBe(OCMe_3)_3 \longrightarrow (Li_2(CMe_3)_2Be(OCMe_3)_2)$

(monomer-dimer equilibrium)

$Et_2Be + NaOCMe_3 \xrightarrow{Et_2O} (NaEt_2Be(OCMe_3)_2)_2$

$Et_2Be + LiOCMe_3 \longrightarrow (EtBeOCMe_3)_{2-3}$

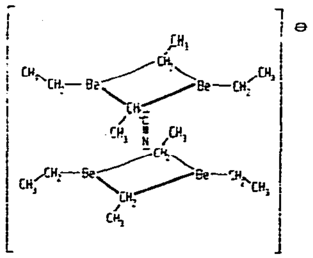
$Et_2Be + RbOCMe_3 \longrightarrow Rb_2Et_3Be_2(OCMe_3)_3$

also:

$Me_3CLi + Be(NMe_2)_2 \longrightarrow (Li(CMe_3)Be(NMe_2)_2)_x$

The potassium complex, $KEt_2Be(OCMe_3)_2$, was found to metalate benzylic hydrocarbons such as toluene and mesitylene (8).

The vibrational spectrum and the proton NMR spectrum of $[Me_4N][(Et_2Be)_2CN(BeEt_2)_2]$ have been obtained (9). The novel sandwich structure 4 was proposed on the basis of their evaluation.



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The following items merit mention:

Ab initio calculations for the ground state of the species CH_2Be (10).

The preparation of HBeCl by the reaction of aluminum hydride with beryllium chloride in diethyl ether and by redistribution between beryllium hydride and beryllium chloride (11). This stable, dimeric (in ether) species could find application as a hydroberyllation reagent.

A study of beryllium borohydrides of type $ROBeBH_4$ (12).

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