BERYLLIUM

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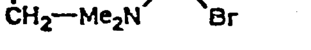
Two reviews dealing with the organic compounds of beryllium and their complexes have been published (1,2).

A useful new route to dialkylberyllium compounds based on the readily available trialkylboranes has been developed by Coates and Francis (3):

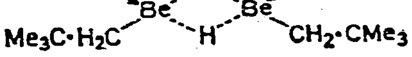
$$2\ R_3B + 3\ Et_2Be \longrightarrow 2\ Et_3B + 3\ R_2Be$$

(R = n-Pr, i-Bu, Me_3CCH_2, Me_3SiCH_2)

Dineopentylberyllium was found to be partly associated in benzene. $(Me_3SiCH_2)_2Be$ is dimeric in this solvent and forms an orange-red, stable 1:1 complex with 2,2'-bipyridine. The reaction of diethylberyllium with sec-Bu_3B gave insoluble, crystalline Et_3Be_2H rather than the expected sec-Bu_2Be, presumably via dehydroberyllation of the $Et_3Be_2CHMeEt$ intermediate. Complexes of neopentylberyllium compounds have been described by the same authors (4): $R_2Be \cdot OEt_2$, $R_2Be \cdot NMe_3$, $R_2Be \cdot TMED$, $RBeBr \cdot TMED$ $\boxed{1}$, and $(RBeH)_2 \cdot TMED$ $\boxed{2}$. The action

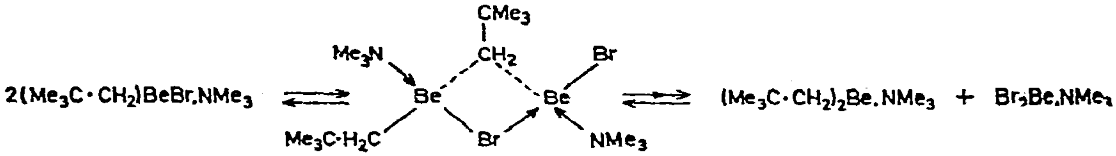


$\boxed{1}$



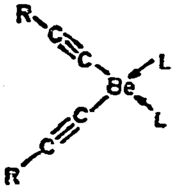
$\boxed{2}$

of trimethylamine on Me_3CCH_2BeBr resulted in disproportionation:



A mixed alkyl complex, $MeBeCH_2CMe_3 \cdot TMED$, also was isolated.

The organolithium route served in the preparation of $(MeC{\equiv}C)_2Be$ and $(Me_3CC{\equiv}C)_2Be$ (5). Both were insoluble and probably polymeric in the unsolvated state. They were found to react with Lewis bases to form three types of complexes, $\boxed{3}$, $\boxed{4}$, and $\boxed{5}$. For those of type $\boxed{3}$, examples with



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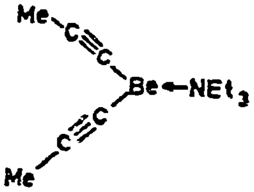

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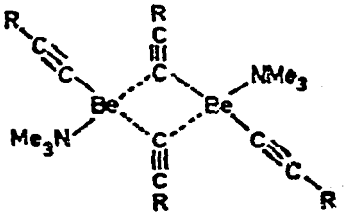
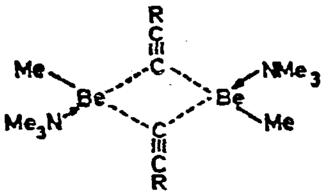


$\boxed{5}$

L = NMe_3, THF and pyridine were described. The steric bulk of the triethylamine molecule restricted this base to the formation of $\boxed{4}$. The dimeric complexes $\boxed{5}$ were of special interest. Both (R = Me and Me_3C) reacted with $Me_2Be \cdot NMe_3$ to give $\boxed{6}$. The structure of $\boxed{6}$ (R = Me) has been determined



$\boxed{6}$

by X-ray crystallography (6), and the molecular geometry and dimensions are shown in Fig. 1.

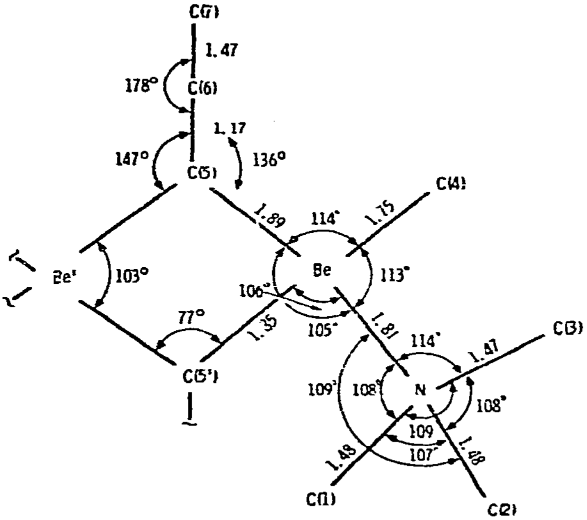
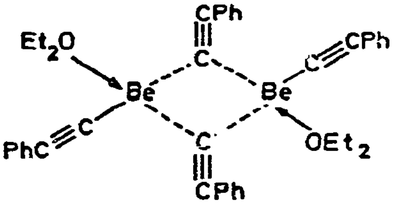


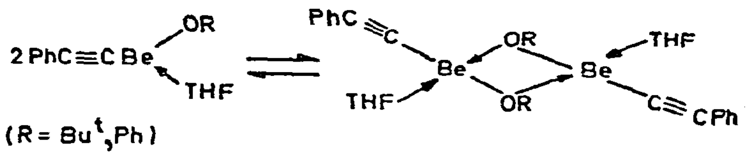
Fig. 1. Labels of atoms used in methyl-1-propynylberyllium–trimethylamine dimer. Only one half of the centrosymmetric molecule is shown. (6)

Various complexes of bis(phenylethynyl)beryllium of type $(PhC{\equiv}C)_2Be \cdot 2L$ (L = py, THF, $MeNH_2$, Me_2NH, Me_3N, $PhNH_2$) and $(PhC{\equiv}C)_2Be \cdot L\text{-}L$ (L-L = TMED, bipy, DME) have been prepared and studied (7). $(PhC{\equiv}C)_2Be \cdot NMe_3$ is monomeric in benzene, but the diethyl ether adduct is associated (n = 1.6-1.7). The dimer is believed to have structure $\boxed{7}$. The action of

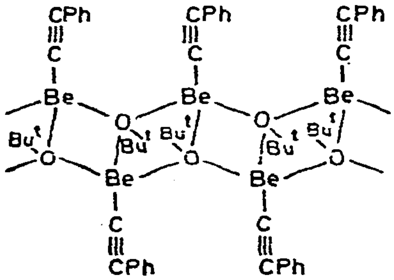


$\boxed{7}$

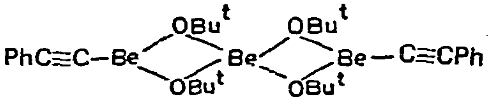
phenylethynyllithium on $(PhC{\equiv}C)_2Be \cdot 2THF$ gave the insoluble $Li_2Be(C{\equiv}CPh)_4$. Partial cleavage of $(PhC{\equiv}C)_2Be \cdot 2THF$ by t-butanol and by phenol produced compounds of type PhC≡CBeOR•THF which in benzene solution were present as an equilibrium mixture of monomer and dimer:



Uncomplexed PhC≡CBeOCMe$_3$ was insoluble in benzene and remarkably inert chemically, being stable to water, 2N or methanolic H_2SO_4, ethanolic NaOH and acetic acid. A polymeric structure, $\boxed{8}$, was suggested. Another butoxide of structure



$\boxed{8}$



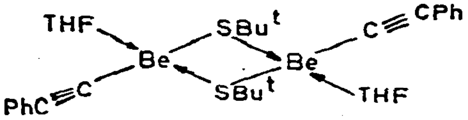
$\boxed{9}$

$\boxed{9}$ could be prepared via two different reactions:

$$3(PhC{:}C)_2Be,NEt_3 + 4Bu^tOH \longrightarrow (PhC{:}C)_2Be_3(OBu^t)_4 + 4PhC{:}CH$$

$$(PhC{:}C)_2Be,OEt_2 + 2(Bu^tO)_2Be \longrightarrow (PhC{:}C)_2Be_3(OBu^t)_4 + Et_2O$$

The product from the reaction of $(PhC{\equiv}C)_2Be{\cdot}2THF$ with Me_3CSH was dimeric in benzene, $\boxed{10}$.



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The reduction of ketones of type RCOPh (R = Et, i-Pr and t-Bu) with $[(+)\text{-}(R)\text{-}EtMeCH]_2Be$ gave optically active carbinols, R(Ph)CHOH (8). The percent asymmetric induction varied with R: Et, 14.8%; i-Pr, 46%; t-Bu, 30.8%. These results provide support for the hypothesis that such reductions involve transfer of the β-hydrogen of the organometallic reagent to the carbon carbon via a cyclic 6-center transition state, rather than by a dehydrometalation-metal hydride reduction sequence.

The reaction of acylberyllium bromides with aromatic nitro compounds has been described (9):

$$RCOBeBr + ArNO_2 \longrightarrow ArNHCOR + Be_4O(O_2CR)_6$$

The following process is believed to take place:

$$RCOBeBr + ArNO_2 \longrightarrow ArNO + RCO_2BeBr$$

$$ArNO + 2\ RCOBeBr \longrightarrow ArNHCOR + RCO_2BeBr$$

$$2\ RCO_2BeBr \longrightarrow BeBr_2 + (RCO_2)_2Be$$

$$4\ (RCO_2)_2Be \longrightarrow Be_4(O_2CR)_8 \longrightarrow Be_4O(O_2CR)_6 + (RCO)_2O$$

The molecular structures of methyl(cyclopentadienyl)beryllium and cyclopentadienylberyllium chloride have been determined by gas-phase electron diffraction (10). Both have the "half sandwich" structure with approximately C_{5v} symmetry. Both compounds are monomeric in hydrocarbon solution, possibly, the authors state, because the beryllium atom has an octet of electrons (2 Be electrons, 1 from the σ-bonded ligand and 5 from the C_5H_5 group). Other workers, in considerations of dicyclopentadienylberyllium, suggest that the beryllium atom effects a tunnel (virtual) chemical bond between the cyclopentadienyl rings (11).

A beryllium atom has been incorporated into an icosaderal carborane via reaction of dimethyl- or diethylberyllium diethyl etherates with (3)-1,2-$B_9C_2H_{13}$ in ether/benzene medium (12). The product, $B_9BeC_2H_{11}\cdot OEt_2$ reacted with trimethylamine to displace the ether, giving $B_9BeC_2H_{11}\cdot NMe_3$. The structure shown in Figure 2 was proposed for these compounds.

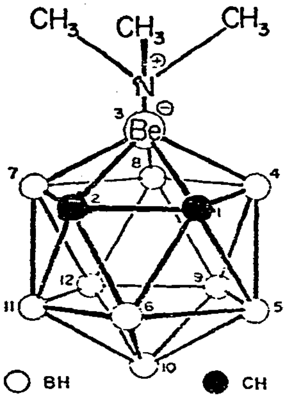

Fig. 2. Proposed structure of (3)-$BeN(CH_3)_3$-1,2-$B_9C_2H_{11}$. The diethyl etherate presumably has same gross structure with $(C_2H_5)_2O$ replacing $N(CH_3)_3$. (12)

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