BERYLLIUM

ANNUAL SURVEY COVERING THE YEAR 1973

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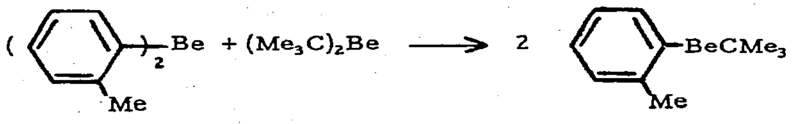
There has been little activity in the area of organoberyllium chemistry during the past year.

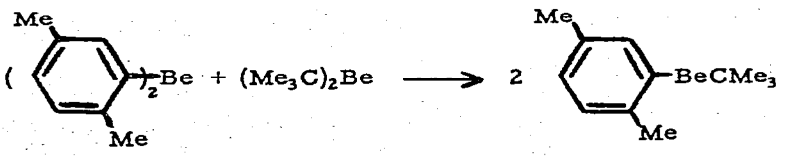
Patents describe the preparation of di-n-butyl- and diisobutylberyllium by the organolithium route and their conversion to beryllium hydride species (1) and the redistribution of dicyclopentadienylberyllium with beryllium hydride in ether to give C_5H_5BeH (2). Coates has continued his work in organoberyllium chemistry with the preparation of unsymmetrical diorganoberylliums by redistribution reactions (3):

$$3/n\ (Me_2Be)_n + 3\ (Me_3C)_2Be \xrightarrow{\text{benzene}} 2\ (Me_3CBeMe)_3$$

$$2\ Et_2Be + 2\ (Me_3C)_2Be \longrightarrow 2\ (Me_3CBeEt)_2 \quad \text{(distillable without disproportionation)}$$



(dimeric in C_6H_6)



(dimeric in C_6H_6)

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$(C_5H_5)_2Be + (Me_3C)_2Be \longrightarrow 2\ C_5H_5BeCMe_3$ (monomeric in C_6H_6)

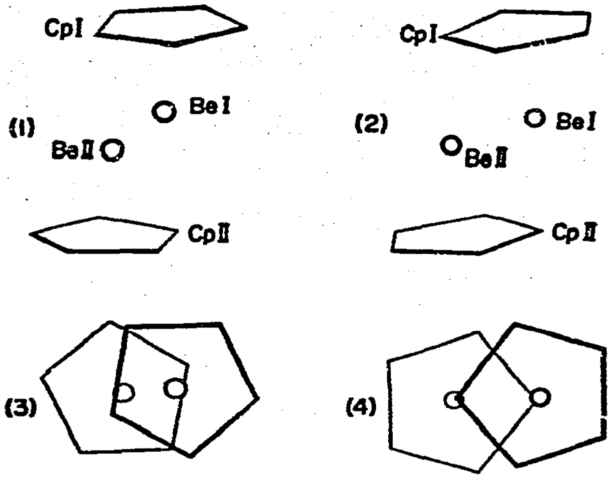
$(C_5H_5)_2Be + (C_6F_5)_2Be \cdot 2THF \longrightarrow 2\ C_5H_5BeC_6F_5$ (monomeric)

Pyrolysis of the $ArBeCMe_3$ compounds provided a route to insoluble hydrides of type ArBeH (Ar = o-tolyl, m-tolyl), while pyrolysis of $(Me_3CBeMe)_3$ at 120° gave insoluble, polymeric MeBeH. Heating a mixture of diethylberyllium and $(Me_3CBeEt)_2$ resulted in formation of the known hydride species Et_3Be_2H. A redistribution of di-t-butylberyllium with beryllium chloride gave t-butylberyllium chloride which was characterized as its insoluble quinuclidine adduct. Complexes of these $ArBeCMe_3$ compounds with TMED were prepared. Glockling has studied the behavior of diphenylberyllium upon electron impact (4). At 200-240°, parent trimer and monomer ions ($Ph_6Be_2^{+\cdot}$, $Ph_2Be^{+\cdot}$) were produced. The standard heat of formation of solid diphenylberyllium was determined to be 36.6 kcal/mol by measurement of the enthalpy of its acid hydrolysis. The mean Ph-Be bond energy thus is about 80.3 kcal/mol.

The crystal structure of dicyclopentadienylberyllium has been determined at room temperature (5) in order to shed some light on the cause for the apparent structural differences between the molecules of this compound in the gas phase and in the solid at -120°. It was found to be a "slip" sandwich; however the rings are neither staggered (as at -120°) nor eclipsed, but somewhere in between (Fig. 1). From the geometry and the beryllium-to-ring carbon atom distances it was concluded that the beryllium atom is π-bonded to one ring and nearly electrostatically bonded to the other ring. It was suggested that the C_{5v} symmetry observed for $(C_5H_5)_2Be$ in the vapor state represents an average of the dynamic, flexibly-bonded "slip" sandwich structure.

The vibrational spectra of di-t-butylberyllium etherates ($t\text{-}Bu_2Be \cdot OR_2$, R = Me, Et) (6) and sulfide complexes ($t\text{-}Bu_2Be \cdot SR_2$, R = Me, Et) (7), as well as of liquid di-t-butylberyllium, have been studied.

Molecular orbital calculations have been performed on MeBeH and



(1), (2) Side View of the Molecules at Room Temperature and at -120° Respectively.

(3), (4) Top View at R.T. and L.T.

Figure 1. Structures of Dicyclopentadienylberyllium at Room Temperature and at -120° (from C. Wong et. al, Inorg. Nucl. Chem. Lett., 9 (1973) 667)

H_2NBeH and their dimers (8), as well as on dicyclopentadienylberyllium (9).

A further paper on the chemistry of acylberyllium halides described the action of $CH_3C(O)BeBr$ on aromatic aldehydes to produce the trans-stilbenes (10).

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