BERYLLIUM

ANNUAL SURVEY COVERING THE YEAR 1972

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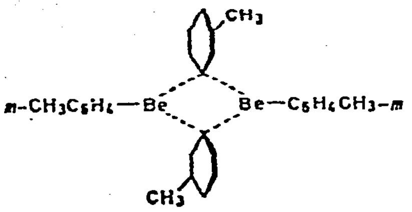
Coates and Srivastava (1) prepared diphenylberyllium in high yield by two procedures:

$$Et_2Be + Ph_2Hg \longrightarrow Et_2Hg + Ph_2Be$$

$$3\ Et_2Be + 2\ Ph_3B \longrightarrow 2\ Et_3B + 3\ Ph_2Be$$

and have applied the latter exchange process to the preparation of other Ar_2Be compounds ($Ar = p\text{-}ClC_6H_4$, $o\text{-}MeC_6H_4$, $m\text{-}MeC_6H_4$, $2,5\text{-}Me_2C_6H_3$, $1\text{-}C_{10}H_7$). Steric hindrance appears to be responsible for the lack of similar exchange between diethylberyllium and trimesityl-, triisopropyl-, tricyclopentyl- and tricyclohexylborane, but other factors must cause tribenzylborane to be inert to diethylberyllium.

The ditolylberylliums and the dixylylberyllium thus prepared were found to be dimeric in benzene, presumably as a result of aryl group bridging $\boxed{1}$ (1). Various adducts of these and other diarylberylliums with Lewis bases were characterized (1), e.g., $(1\text{-}C_{10}H_7)_2Be \cdot 2py$, $Ph_2Be \cdot Me_2NCH_2CH_2NMe_2$, $(o\text{-}MeC_6H_4)_2Be \cdot NMe_3$, $(C_6F_5)_2Be \cdot Me_2NCH_2CH_2NMe_2$ (via C_6F_5Li), $(Mesityl)_2Be \cdot NMe_3$ (via the Grignard reagent), $(C_6F_5)_2Be \cdot 2py$, $(PhCH_2)_2Be \cdot OEt_2$ (via $PhCH_2$-



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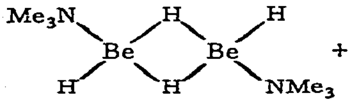
MgCl), (m-$MeC_6H_4)_2Be\cdot MeOCH_2CH_2OMe$, and others. A crystalline ate complex, $LiBe(o\text{-}MeC_6H_4)_3$, also was described.

Dialkylberyllium compounds were found to react with benzonitrile, showing both alkylation and reduction activity (2):

$$(Me_3C)_2Be + PhC{\equiv}N \longrightarrow \xrightarrow{H_3O^+} PhCH{=}O + Ph(Me_3C)C{=}O$$

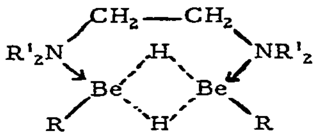
Alkylation was favored (91:9) by lower (30°) temperatures. An increase in the temperature to 67° gave a product mixture containing 86% benzaldehyde and only 14% of the alkylation product. Similar alkylation of benzonitrile with di-(R)-2-methylbutylberyllium gave (+) (S)-1-phenyl-3-methylpentan-1-one in 95% optical purity.

A number of complexes of alkylberyllium hydrides with tetramethylethylenediamine (TMED), $(RBeH)_2\cdot TMED$ (R = sec-Bu, t-Bu, n-C_5H_{11}, Ph, o-MeC_6H_4) have been prepared by reaction of the RBeCl compounds with lithium hydride, followed by addition of TMED (3). Similar tetraethylethylenediamine (TEED) complexes were prepared, $(RBeH)_2\cdot TEED$ (R = Me, Ph), and a pentylberyllium hydride complex was obtained by an olefin addition reaction:



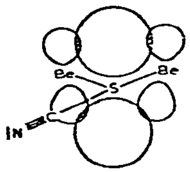
$$+\ n\text{-}C_3H_7CH{=}CH_2 \xrightarrow{C_6H_6} (C_5H_{11}BeH\cdot NMe_3)_2$$

The $(RBeH)_2 \cdot TMED$ (R = alkyl) complexes are monomeric in benzene and structure $\boxed{2}$ was suggested. Diethylberyllium was found to



$\boxed{2}$

react with tetramethylammonium thiocyanate to give the anionic complex $Me_4N[(Et_2Be)_2SCN]$ (4). The vibrational and proton NMR spectra of this complex indicate that both diethylberyllium molecules are bonded to sulfur. It was suggested that additional overlap between a filled sulfur orbital and vacant Be p orbitals contributes to the bonding:



The vibrational spectra of liquid, freshly distilled, dimeric diethylberyllium (4) and of di-t-butylberyllium in the gaseous, liquid and solid state (5) have been reported.

Several structural studies have dealt with cyclopentadienylberyllium compounds. The crystal structure of bis(cyclopentadienyl)-beryllium at -120° (6) is shown in Fig. 1. This remarkable "slipped sandwich" structure, which was described by the authors in terms of a π-σ formulation but in terms of a π-slipped π formulation by Drew and Haaland (7), is not present in $(C_5H_5)_2Be$ in the vapor state (7). Gas phase electron diffraction has been used to determine the structure of

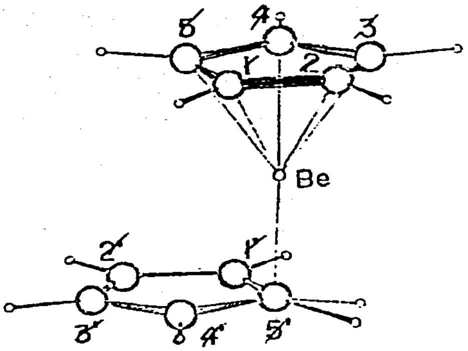


Fig. 1. The ordered molecular configuration of $Be(C_5H_5)_2$ at -120°C. (from Wong et al., Acta Cryst. B28 (1972) 1662).

of $C_5H_5BeCH_3$ (Fig. 2) (8) and C_5H_5BeCl (Fig. 3) (9). The microwave spectrum of C_5H_5BeCl confirmed the C_{5v} symmetry and demonstrated a dipole moment of 4.26±0.16D (10). The bonding in $C_5H_5BeCH_3$ and C_5H_5BeCl was described in terms of sp-hybridized beryllium involved in simple σ-type overlap with CH_3 or Cl and overlap also with the $a_{1\pi}$ MO of the C_5H_5 ring. Further bonding involves the two two unhybridized Be 2p orbitals in π-type overlap with the filled $e_{1\pi}$ C_5H_5 MO orbitals, forming two degenerate bonding MOs.

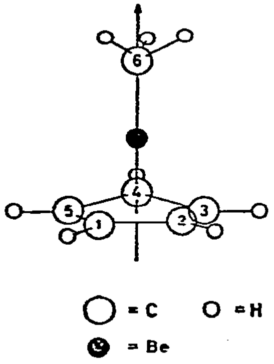


Figure 2. Structure of $C_5H_5BeCH_{3(g)}$. (from D. A. Drew and A. Haaland, Acta Chem. Scand., 26 (1972) 3079)

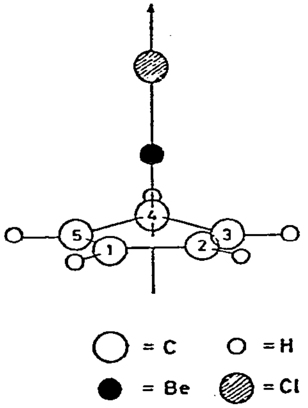
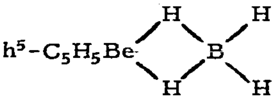
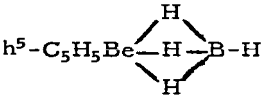


Figure 3. Structure of $C_5H_5BeCl_{(g)}$. (from D. A. Drew and A. Haaland, Acta Chem. Scand., 26 (1972) 3351)

A gas phase electron diffraction study could not distinguish between two possible structures of $C_5H_5BeBH_4$ (11):



and



Although they do not deal with strictly organometallic compounds, we mention investigations of sterically hindered beryllium alkoxides (12) and t-butoxyberyllium halides (13):

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