BERYLLIUM

Annual Survey Covering the Years 1979-1981[*]

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1. CALCULATIONS

As noted by Seyferth[1] in the previous review for 1977 and 1978, the majority of papers on beryllium chemistry are theoretical in nature. A major survey of theoretical work has appeared which give a brief summary of all of the papers which appeared prior to 1981.[2]

Böhm, et al.[3] have used CNDO methods to calculate group molecular orbital electronegativities for a variety of first period radicals including BeH, $BeCH_3$, BeF, BeCl, and BeBr. The respective values on the Pauling scale are 1.06, 1.29, 2.67, 1.43, and 1.19. The recent reports include CNDO/2 calculation on beryllium acetylacetonate in an attempt to explain the donor-acceptor and bonding of the chelate ring to beryllium and to explore the role of the d-orbitals of non-transition metals on bonding.[4]

Studies on a wide variety of beryllium hydride derivatives have been reported. Pyykkö[5] has examined BeH^+ and the linear BeH_2 systems, along with a number of others, using relativistic and non-relativistic Hartree-Fock one-center expansion calculations. "Molecular" covalent radii, consistent with Pauling's halogen radii, are deduced for all the elements considered. In other studies, the band structures of linear $(BeH_2)_n$ was described using ab initio techniques.[6] The results reported indicate that the double-degenerate valance band has π symmetry and is composed of a Be p orbital and an antisymmetric combination of the H 1s orbitals. The charge distribution indicates that the hydrogen atoms carry a small (less than 0.1 electron) negative charge. Similar studies were carried out on HBX species (X = Be, BH, CH_2, NH, O) in which the conduction band was shown to have π-symmetry with the energy gap increasing in the order given for the substituent groups.[7]

Several papers have appeared in the Russian literature in which the formation, energy surfaces, and structures of $LiBeH_3$, and the related $LiBeX_3$ derivatives, have been examined.[8-12] They concluded that there is no energy barrier for either the reaction of hydride or LiH with BeH_2 and suggested that the most stable form of the $LiBeH_3$ involves the formation of the simple complex; I. They also carried out calculations on the series $LiBeF_3$, $LiBeH_3$, and $LiNO_3$ and reached the same conclusion.[12]

They suggested that the Li atom has a significant barrier to migration in these systems. This same group[13,14] investigated the potential surface and structure of Li_2BeH_4 based on calculations using the Hartree-Fock-Roothaan method with a 2-
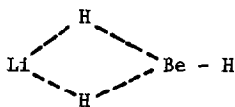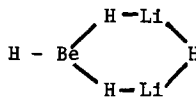

I

exponential basis set. They found that the classical structure, II, was ∿2.5 kcal/mol higher in energy than the cyclic, planar structure, III. Würthwein, et al.[15] also have examined these systems and have reached essentially the same conclusion for the $LiBeX_3$ species. For the Li_2BeH_4 system, their highest level of calculation suggest
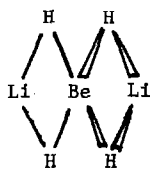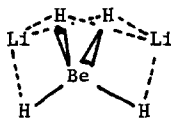

II

III

that III represented the second most favorable species energetically. The most favorable structure, from their calculations is shown in IV, in which the lithium atoms are attached to two of the faces of the tetrahedral BeH_4 unit. They examined the energies of other possible geometries and of a variety of dissociation processes for


IV

these systems. The Russian group has studied these systems in a continuation of their work and have examined the structure, energy, and rigidity of a variety of complexes, included $BeBH_4^+$, $HBeBH_3^+$, $HBeBH_4$, and $Be(BH_4)_2$, as well as the related Mg derivatives, by means of ab initio calculations.[16] INDO calculations were carried out on the latter compound, $Be(BH_4)_2$, to determine the barriers to various internal motions and to obtain structures for the stable forms.[17] Calculations also were carried out on the beryllium hydride species, Be_2H_4 and $[Be_2H_3]^+$. The equilibrium geometry of Be_2H_4 is a flat bridged configuration of symmetry D_{2h} while the ion is linear.[18] Marynick[19] reported extensive theoretical calculations on the electronic structure of polymeric beryllium borohydrides in the solid state. He compared his results with experimentally determined parameters obtained from crystallography and

infrared spectroscopy. The two significant conclusions reached are that, for the system $(BeB_2H_8)_n$ the solid state parameters can not be effectively calculated for $n = 3$, but by the time $n = 6$ the calculations are in good agreement with the experimental parameters for the solid state. Further, the model which best describes the solid may be viewed as ionic, $(BeBH_4)^+$, $(BH_4)^-$, with small covalent interaction between the ions.

Calculations have been reported on a wide variety of Be-C bonded species. These include the investigation of the interaction of CO with Be^{+2} and Be by CNDO methods.[20] The calculated minimum energy geometries were linear and triangular respectively with the Be-CO and C-O bond energies of the same order at about 180 kcal/mol in the $BeCO^{+2}$ complex. In BeCO, the Be-C interaction energy is calculated to be 80 kcal/mol and the energy for excitation of CO is lowered, consequently lowering the energy necessary for activation of CO.

Calculations have been made on the interaction of metal ions of group I and II, including Be^{+2}, with S-S bonded systems to explore the formation of stable complexes and the electrophilic cleavage of this unit.[21] The calculations indicated the Be^{+2} formed stable complexes of the form indicated in V with the monocoordinated species

V   VI
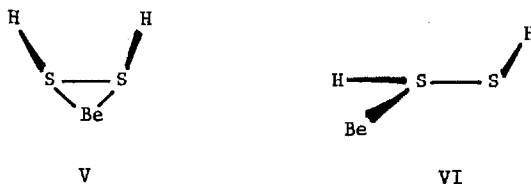
in VI ~12 kcal/mol higher in energy. Further Be^{+2} was the only ion found to be exothermic for the cleavage reaction or to compete with H^+ to form stable S-bonded complexes in aqueous systems. An extensive discussion of possible reaction paths, based on these calculations, was presented.

Pross and Radom[22] have carried out calculations on the isoelectric series XNH_3^+, XCH_3, and XBH_3^- at the 4-31G level where X = Li, BeH, BH_2, NH_2, OH and F. The results indicate that the energies are dominated by σ effects with favorable interaction of the BeH σ donor with NH_3^+ and unfavorable interaction in XBH_3^-. The range of interaction energies with CH_3 is relatively narrow compared to that for the other species. Subsequent calculations on systems of the type XCH_2^- and XCH_3, where X = Li, BeH, BH_2, etc., were carried out and indicate that the vacant orbital on BeH interacts strongly with the electron pair on the CH_2^- fragment.[23] This also was found for XCH_3 resulting in increased acidity of the protons on carbon. The results were predicted qualitatively both at the 4-31G and 6-31G levels with improved, though still imprecise, quantitative results in the latter case.[23] Calculations on five coordinate carbon species of the form $CH_3X_2^+$(X Li, BeH, Na, MgH) indicate that

a D_{3h} structure with a linear 3 centered 2 electron bond, as shown in VII, is favored.[24] Similar results are obtained for the lithium species. In both cases these are discussed with respect to their importance in electrophilic substitution reactions. This group has carried out calculations of this type on the anions of the form CH_2X^- for the Li to F period and reported that the vacant p orbital on BH_2, BeH, and even Li, interact strongly with the available electron pair on the CH_2 moiety stabilizing the systems.[25] Dill, et al.[26] have carried out calculations which show the nature of the effect of BeH on strained systems such as cyclopropane. They concluded that the dominant effect is inductive for BeH on strained systems such as
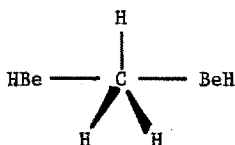
VII

cyclopropane. They concluded that the dominant effect is inductive for BeH and that BeH is less stabilizing that Li. They did only limited studies because of the slow convergence of the calculations.

Studies by Dewar, et al.[27] on a variety of pentadienyl systems indicated that the BeH^+ altered the preferred geometry to make the U shaped conformation the most stable as indicated in VIII. The stabilization arises from the vacant orbital on the BeH^+ moiety interacting with the π electrons of the terminal group.
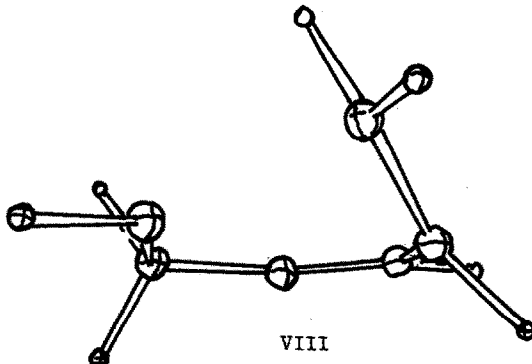
VIII

Dewar and Rzepa[28] have reported a series of calculations using MNDO SCF-MO calculations on half sandwich complexes of BeH^+ and $BeCl^+$ with indenyl and fluorenyl anions. Three stable isomers were located for the indenyl beryllium hydride or chloride systems corresponding to η^6, η^5, or η^1 interactions with the stability increasing in the order given. It was noted that the MNDO approach may give energies too high for these systems with extensive delocalization. For the fluorenyl system only η^6 and η^1 were found to be stable with the η^1 isomers (Be atom located at the 9

position) by far the most stable.

There have been a number of studies which deal with the interaction of Be or BeX species with cyclopentadiene or related aromatic ring systems. These include several papers in the Russian literature which provide information concerning the energies of interaction between the C_5H_5 ring and Be species. CNDO/2 procedures were used to calculate energies of atomization,[29] bond lengths, and geometries.[30] Calculations also were carried out using several different basis sets and in each case the minimum energy corresponded to the symmetrical D_{5h} structure for berylocene, BeCp, as shown in IX.[31]
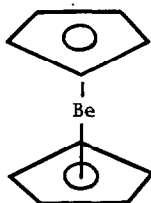
IX

Extensive calculations, employing the PRDDO program, were made on $B_5H_{10}BeX$ derivatives where X = BH_4, B_5H_{10}, Me, or C_5H_5 by Bicerano and Lipscomb.[32] The bonding in these systems was analyzed in terms of charge stability, static reactivity indinces, degrees of bonding, overlap populations, and fractional bonds obtained from localized molecular orbitals by using the criterion of Boys. The bonding in the B_5H_{10} units is similar, although the bonding about Be in $B_5H_{10}BeC_5H_5$ differs significantly from that in the other compounds as a result of the ability of C_5H_5 to enter into multiple bonding and to delocalize the electrons about the ring. The results were compared with the limited experimental data available.

Glidewell[33] and, in a subsequent paper, Bews and Glidewell[34] have explored the structure, bonding, and energies in a variety of beryllium species through the use of MNDO calculations. In the first paper, the bonding of the species $Be(CN)_2$, $Be(C\equiv CH)_2$, HBeCN, and $HBeC\equiv CH$ were all found to be linear with the HOMO shown to have π symmetry spanning the heavy atoms with the exception of HBeCN where it is Σ^* concentrated primarily on the HBe bond. Additional calculations were reported on $Be(C_5H_5)_2$ and $(C_5H_5)BeX$ with the conclusions reached that the beryllocene minimum energy configuration is for the D_{5d} symmetry model (see below). In other calculations the molecule, $MeBe_2H_3$, was treated with the minimum energy configuration obtained for the model shown in X in which the three hydrogen atoms form Be-H-Be bridge bonds. For the beryllium substitued methane derivatives, $CH_{4-n}(BeH)_n$, the optimal structures calculated for $HC(BeH)_3$ and $C(BeH)_4$ were planar at carbon. A result which will be of most interest if an experimental test can be made.
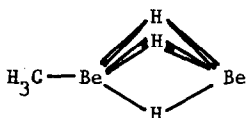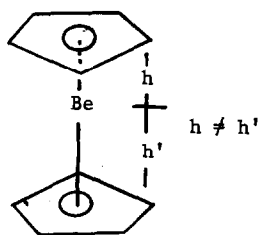
X

The second paper[34] focussed on two areas, the first on calculations of the geometries and bonding for a series of $Be(C_nH_n)_2$ (n = 4-8) derivatives to determine the hapticity of bonding between the ring and Be atom and the second on a series of hetrocyclic systems containing beryllium in the ring.
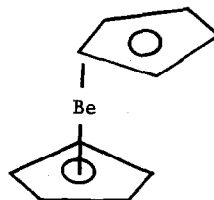
Marynick[35] has examined the energies of a variety of beryllium species of the form $R^tBeR_2{}^bBeR^t$ and the corresponding monomers, R^tBeR^b, by detailed molecular orbital studies where R^t = H, CH_3, F, BH_4, C_5H_5, and phenyl and R^b = H, CH_3, or phenyl. The effect of the substituent in the R^t position was measured by calculating the ΔE's for dimerization and comparing them to that for R^t = H. The C_5H_5 groups were shown to strongly disfavor dimerization, while Me or F substituents in the terminal site, slightly destabilizes the dimers. It also was found that phenyl bridges were highly favored over methyl bridges. These effects were rationalized by examining the various orbital interactions, especially, those which involve the vacant orbitals on Be and their ability to interact with π electron systems.

2. Experimental Studies

The beryllium derivatives most studied by experimental techniques are those which contain a C_5H_5 moiety. Almenningen, et al.[36] have redetermined the structure of beryllocene, $BeCp_2$, in the gas phase by electron diffraction techniques. They concluded that the original proposal of a C_{5v} structure as seen in XI still gives the best fit, but that an acceptable fit of the data can be obtained with the "slip sandwich" model shown in XII. Neither the D_{5d} model nor the σ-π could be brought into


XI

XII

satisfactory agreement with the experimental data.

This system also has been extensively explored by ab initio M.O. calculations (also see above) on five different models with fixed geometry with the lowest energies obtained for π-Cp, σ-Cp model and the D_{5d} model.[37] In the same paper the He(I) photoelectron spectrum of $BeCp_2$ is reported, and the ionization potentials of the first bands are compared with the orbital energies obtained from the M.O. calculations. A satisfactory fit was obtained between experimental and calculated values for a "slip sandwich" model of C_s symmetry as shown in XII. A model with C_{5v} symmetry is only compatible with the PE spectrum if the Jahn-Teller splitting of the lowest $^2E_1$ state of the molecular ion is exceptionally large. The conclusion which was drawn from these results is that some unsymmetrical species such as the π-Cp, σ-Cp or the slip sandwich configuration best describe beryllocene.

The Raman spectra of both solid and liquid $BeCp_2$ have been reported and interpreted in terms of the presence of two π-bonded rings in the molecule, one pentahapto and one polyhapto bound ring.[38] This interpretation corresponds to a form of the "slip andwich" configuration, XII, as given.

The H(I) photoelectron spectra of a series of derivatives CpBeX (X = CH_3, C≡CH, C≡CCH$_3$, Cl, Br) have been reported.[39] The experimental first ionization energies obtained from these studies were compared with those obtained from CNDO-type calculations. Reasonably good agreement was obtained between the experimental and caluclated values. In the latter four compounds, the four lowest energy bands were assigned to two $^2E_1$ states, one arising rom the X ligand and the other from the Cp group with a Jahn-Teller splitting of 0.1-0.2eV.

The preparation and structures of a number of dimeric compounds bridged by N, O, or hydrogen have been reported. Hall, et al.[40] prepared $[BeCl(N=CBu^t_2)]_2$, $Li[Be(N=CBu^t_2)_3]$, $[Be(N=CBu^t_2)]_2$ $BeBu^i(N=CBu^t_2)]_2$, $Be(N=CBu^t_2)[N(SiMe_3)_2]$, $BeBu^i(N=CPh_2)]_2$ and $BeBu^t(N=CPh_2)]_2$. The preparations were carried out making use of the following reaction sequence or suitable modifications of these and are clearly described:

$$1/2[BeCl(N=BeBu^t_2)]_2 = 3LiCl \qquad (1)$$

$$\xrightarrow{Li[N(SiMe_3)_2]} [Be(N=BeBu^t_2)(N(SiMe_3)_2]$$

$$2\ BeCl_2 + 4\ Li(N=CBu^t_2) \qquad\qquad\qquad + LiCl \quad (2)$$

$$[Be(N=CBu^t_2]_2 + 4LiCl \qquad (3)$$

$$\xrightarrow{Li(N=CBu^t_2,} LiBe(N=CBu^t_2)_3 \qquad (4)$$

$$BeBu^i_2 + 2\ Bu^t_2C=NH \rightarrow \quad 1/2[Be(N=CBu^t_2)_2]_2 + 2\ Bu^tH \qquad (5)$$

The compounds were characterized by their IR, ^{1}H NMR, and mass spectra. The X-ray structure of $[Be(N=CBu^t_2)_2]_2$ is reported and schematic representation is shown in XIII. An extensive discussion concerning the Be-N bonding is presented along with a comparison to C, O, and H bridged systems. It was specifically noted that the small Be-N-Be angle results in a short Be-Be distance, but that in this case no additional metal-metal bonding occurs since the N atom formally donates 3 electrons to the bridge system.

A series of cyclic beryllium silylamides has been prepared by reaction of $BeMe_2$
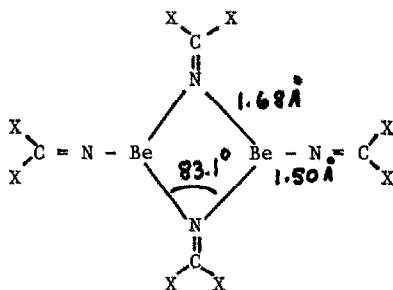
XIII

with the appropriate aminosilane.[41] These are indicated in XIV, XV, XVI, and XVII. In solution and in the solid state, they form dimers and probably higher oligomers

XIV   XV   XVI   XVII
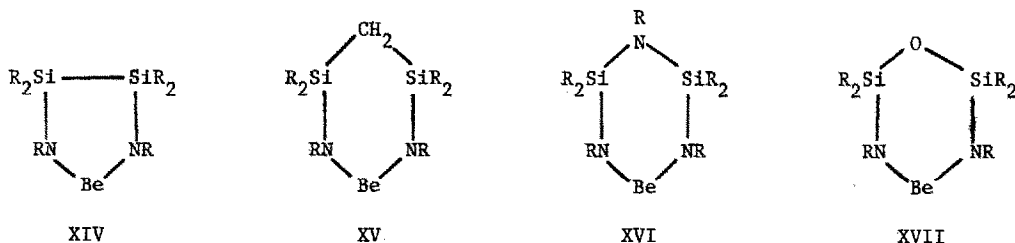
based on their NMR spectral behavior as a function of temperature and solvent. The
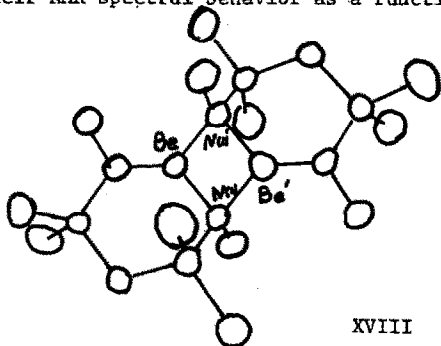
N(1)-Be	1.714 Å
N(1)-Be´	1.683
N(2)-Be	1.550
Be-N(1)-Be´	80.2°
N(1)-Be-N(1)´	99.8°

XVIII

crystal structure of XV has been determined and a diagram is given in XVIII with the significant Be-N distances and angles given.

The structure of the complex, tetra(t-butoxy)triberyllium bis(tetrahydro)borate, $[Be_3(OBu^t)_4(BH_4)_2]$, has been determined in order to provide information concerning the mode of bridge bonding between the borohydride unit and beryllium.[42] A diagram of the structure is given in XIX with some of the pertinent parameters. The most significant feature is that the borohydrides is bridged through 2 hydrogen atoms to the Be fragment.

The structure of disodium di-μ-hydrido-bis(diethylberyllate) diethyl ether sol-
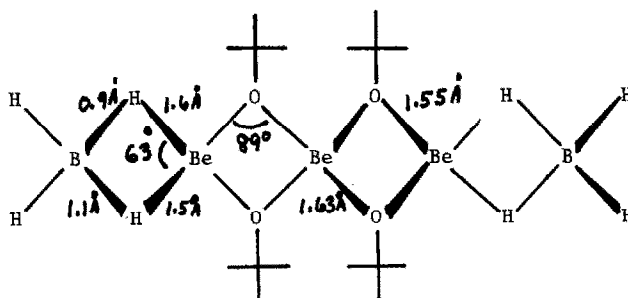
XIX

vate has been reported.[43] A diagram is given in XX. The important features are
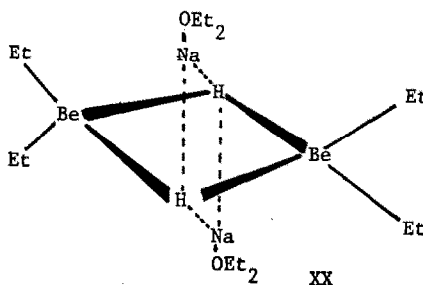
XX

those surrounding the Be-H-Be bridge bonds, the Be-Be distances is 2.2 Å which is ∿0.1 Å greater than that reported in BeMe$_2$, and the average Be-H distance and Be-H-Be angle are ∿1.49 Å and 97°, respectively. The Be-H distance might be compared with the value reported in the previous paper of 1.55 Å keeping in mind the fact that the hydrogen positions are not well determined.

Gaines, et al.[44,45] have reported the preparation, characterization, and structure of μ-[η^5-cyclopentadienylberylla]octahydropentaborate, μ-[η^5-C$_5$H$_5$)Be]B$_5$H$_8$. The compound was prepared by the reaction indicated in 6. The product was

$$KB_5H_8 + (\eta^5\text{-}C_5H_5)BeCl \rightarrow KCl + \mu\text{-}(\eta^5\text{-}C_5H_5)BeB_5H_8 \qquad (6)$$

stable to 80° in C_6D_6 where slow decomposition to undefined products occurred and to 140° in di-n-butyl ether. It did not react with diethyl ether but eliminated Me_3NBH_3 as the only identifiable product on the addition of NMe_3. Reaction with HX produced $(\eta^5\text{-}C_5H_5)BeX$ and B_5H_9. Reaction with $ZnMe_2$ gave $(\eta^5\text{-}C_5H_5)BeMe$ and $(\mu\text{-}CH_3Zn)B_5H_8$. The structure of $\mu\text{-}[(\eta^5\text{-}(C_5H_5)Be]B_5H_8$ is given in XXI and shows that the BeC_5H_5 portion of the molecule is as expected from earlier studies, and that the Be atom serves as a bridge between two of the boron atoms on the base of the B_5 pyramid. The ^{11}B and ^1H NMR of a solution of the compound are consistent with this structure indicating that it does not undergo rearrangement on dissolving. Additional
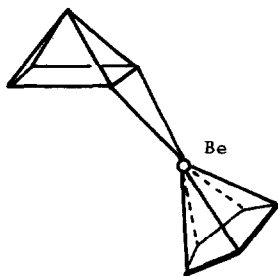
XXI

characterization of the beryllaboranes has been reported making use of ^9Be NMR spectroscopy which was shown to be useful as a means of characterizing these systems.[46]

A variety of other reactions have been explored which involve simple beryllium compounds.[47] The reaction shown in 7 between the Al and Be derivatives yields a

$$(Me_2AlC{\equiv}CMe)_2 + (MeC{\equiv}C)_2Be \rightarrow$$
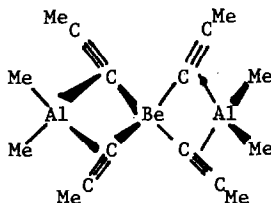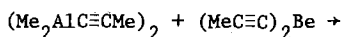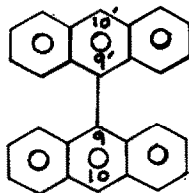

XXII

complex with proposed structure given in XXII has been reported. The structural proposal was based on the NMR and IR data of the product.

Dimethylberyllium has been shown to undergo the reaction given in 8 with formation of the tetrameric product which is presumed to have a cubic structure with Be

$$Me_2Be + (Me_2SiO)_4 \rightarrow (MeBeOSiMe_3)_4. \qquad (8)$$
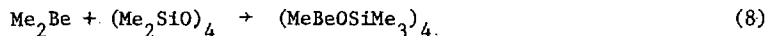
and O atoms at alternate corners of the complex.[48] Reaction with 2-(β-methylamino-ethyl)pyridine gave MeBe[N(Me)C$_2$H$_4$(C$_5$H$_4$N)] while reaction with Me$_2$PH gave uncharacterizable products. In the same paper it was shown that MeBeH and EtBeH add to PhC≡N to yield the tetrameric products (MeBeN=C$^H_{Ph}$). Again, the structure probably has a central unit of Be and N atoms which form a distorted cubic arrangement.

Reaction of the anthracene anion radical with BeCl$_2$ in THF give a crystalline

XXIII

polymeric product which yield 9,9',10,10'-tetrahydro-9,9'-bianthryl on hydrolysis.[49] Hydrolysis with D$_2$O gives exclusively _trans_-10-d, _trans_-1-10'd hydrocarbon implying the beryllium was bound to these sites in the original product. Reaction of anthracene dianion with BeCl$_2$ in THF leads to cleavage of the solvent and formation of _cis_-9,10-dihydro-9,10-bis-(4-hydroxybutyl)anthracene. Comparable reactions with cyclo-octatetraene dianions are discussed.

BePh$_2$ has been shown to react with pyrazine in THF in the presence of Na or K to yield complexes of the form shown in XXIV.[50] This 2:1 radical complex was characterized by its ESR spectrum and the coupling to ^{9}Be. Similarly, the 2:1 complexes could
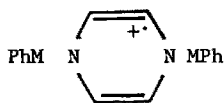

XXIV

be obtained for both Zn and Mg but Mg also formed 1:1 complex.

The reactions given in 9 has been shown to yield the interesting hetrocyclic product XXV in which the Be atom is incorporated in a ring with four coordination.[51] It also was reported that the reaction given in 10 yielded the cyclic product XXVI which contained a four coordinate tetrahedral Be atom as the final product.[52] The latter was characterized by MS and NMR spectroscopy.

The kinetics of the process indicated in eq. 11 have been reported for a variety of complexes where R = Me, Pr^1, PhCH$_2$; R' = 3-NO$_2$, 5-NO$_2$, 5-Br and 5,6-benzo.[53] The mechanism for enantiomerization (inversion of the metal center) of the bis(salicylal-dimates) was suggested as going through a mechanism involving dimerization.

(9)

(10)

+LiCl

(11)

D   L
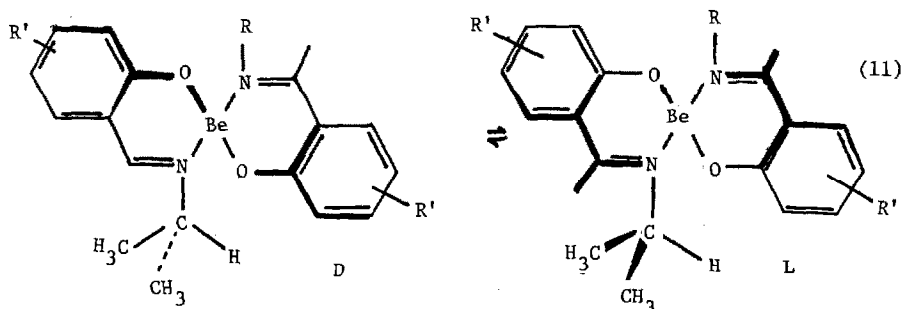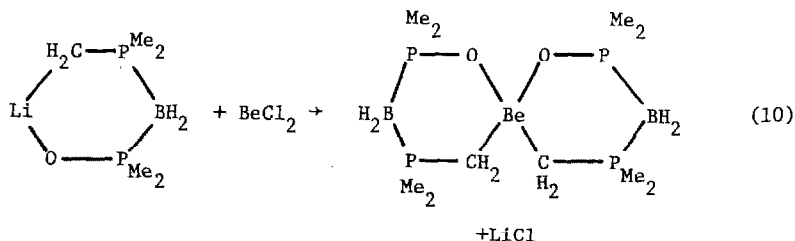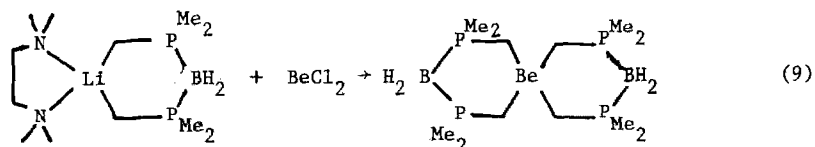
A series of group II bis(isobutynylketonate) complexes of group II metals, including Be, (XXVII) have been prepared and characterized.[54] Based on NMR studies it was suggested that they favor a pseudo-tetrahedral D_{2d} idealized symmetry. Attempts to determine the energy of enantiomerization (inversion at the metal center) were unfruitful apparently due to accidental isochrony of the isopropyl methyl groups in all the temperature ranges investigated.

R = Me, Ph

XXVII
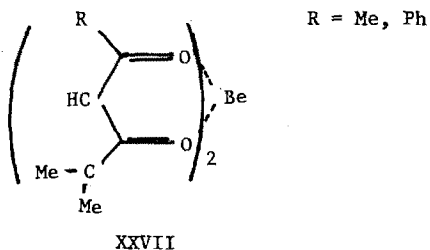
In an extensive study Yasuda, et al.[55] have examined the chemistry and NMR spectra of a variety of dienyl anions. They prepared these derivatives by metal exchange and showed that the Be derivatives existed primarily in the E form as shown in XXVIII for the pentadiendyl derivatives. The uncomplexed species or the weakly complexed derivatives are fluctional with rapid 1-3 migration of the metal occuring. Upon formulation of the TMEDA complex the fluctional behavior is stopped as a result
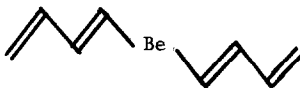
XXVIII

of the coordination of the metal center. Similar results were obtained for other derivatives with variation observed in the ratio of the E and Z species present in solution. For the cyclic systems such as bis(2,4-cycloheptadienyl)beryllium rapid $1 \to 5$ migration was proposed to account for the averaging process observed in the NMR spectrum.

Laplin, et al.[56] have reported that Be reacts with AcBr to yield AcBeBr which then could be reacted with trans-RCH=CHCHO (I, R = Ph, O- and p-MeOC$_6$H$_4$, 3,4-(MeO)$_2$-C$_6$H$_3$, p-BrC$_6$H$_4$ in refluxing EtOAc to give 45-55% p-R$_2$C$_6$H$_4$ and $\leq$9% all-trans R(CH=CH)$_3$R via the intermediate RCH-CHCH. The reaction of I (R = 2-4-Cl$_2$C$_6$H$_3$) with AcOBeBr gave 64% of all-trans-R(CH=CH)$_3$R.

Reaction of Cp$_2$MH$_2$ (M = Mo, W) with BeX$_2$ (X = Cl, Br, I) was reported to give stable addition compounds of the form Cp$_2$MH$_2$·BeX$_2$.[57] Treatment of these with DMF or Me$_2$SO was reported to yield complexes containing these ligands of the form Cp$_2$MH·BeX$_2$.

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