Contribution from the Department of Chemistry,
University of Wyoming, Laramie, Wyoming 82070

Synthesis and Spectroscopic Properties of Cyclopentadienyl(methyl)beryllium and Cyclopentadienylberyllium Halide Complexes

DOUGLAS A. DREW*[1] and GEORGE L. MORGAN

Received November 19, 1976 AIC60830V

Dicyclopentadienylberyllium reacts with dimethylberyllium or beryllium halides in the absence of solvent to form mixed C_5H_5BeX complexes. The products are stable toward disproportionation and monomeric in solution and vapor phases. NMR, IR, and mass spectral data are presented. The bonding interaction between beryllium and the cyclopentadienyl ring is discussed.

The preparation and characterization of mixed alkyl (RMR′) and alkylmetal halides of the group 2 metals have received much attention in the literature. Redistribution reactions between dialkyl and diaryl compounds of mercury[2,3] and magnesium[4] have been investigated. The mercury alkyls will exchange groups in the absence of solvent, and when the exchanging ligands are quite dissimilar (alkyl–aryl), the equilibrium lies far in favor of the mixed species. House and co-workers[4] prepared cyclopentadienyl(methyl)magnesium by a redistribution reaction in ether solvents. Ashby and Parris[5] prepared and isolated a monoetherate of cyclopentadienyl(methyl)magnesium which is reported to be associated in the solid and in benzene solution through methyl bridges. Unsolvated, the compound retains the methyl bridge bonds.

Relatively little information is reported concerning the preparation of mixed complexes of beryllium. Dimethyl-, diethyl-, and diphenylberyllium react with beryllium halides in ether solvents forming mixed species observed via NMR.[6] Bell confirmed that diethylberyllium and beryllium chloride exchange groups in ether through the precipitation of a bipyridyl adduct.[7] The diethyl ether complex of *tert*-butylberyllium chloride (or bromide) is obtained as a by-product from the separation of ether from di-*tert*-butylberyllium etherate by treatment with anhydrous beryllium halide.[8] The complex is dimeric in benzene with bridging halide atoms and monomeric in diethyl ether, complexing with 2 mol of the solvent.[9]

The authors chose to investigate redistribution reactions involving $(C_5H_5)_2Be$ for several reasons. The monomeric nature of this complex suggests low association of mixed species containing the cyclopentadienyl ring. Dicyclopentadienylberyllium is soluble in hydrocarbon solvents allowing the possibility of forming mixed complexes in the absence of ether solvents. The inherent differences between the cyclopentadienyl group and other alkyl or halide groups would tend to favor mixed product formation. Finally, the success with analogous reactions of magnesium was encouraging considering the similarities between the two metals. In addition, $(C_5H_5)_2Be$ has been shown to be a highly unusual complex. It is monomeric in benzene but has a dipole moment of 2.46 ± 0.06 D.[10] Electron diffraction measurements on the vapor show the rings to be parallel with the beryllium atom on the fivefold symmetry axis, considerably closer to one of the rings (1.48 vs. 1.98 Å).[11] The crystal structure of the solid is similiar except that the ring farthest from the metal is slipped 1.20 Å sideways.[12] The vapor-phase infrared spectrum has been interpreted to consist of purely ionic bonding between a beryllium cation and cyclopentadienide anions.[13] It was anticipated that the study of mixed complexes, C_5H_5BeX, would lead to a better understanding of the beryllium–ring bonding interaction.

The reactions pertinent to this investigation are represented by eq 1. The formation of $C_5H_5BeCH_3$ was observed in

$$(C_5H_5)_2Be + BeX_2 \rightarrow 2C_5H_5BeX \quad (1)$$

$$X = CH_3, Cl, Br, I$$

reactions with benzene as solvent via NMR and IR spectra. Separation of the complex from solvent was difficult due to the high volatility of the product. Fortunately, the exchange process occurs readily with *no* solvent present and the high volatility of the mixed species afforded easy separation and isolation from starting materials. Solvent-free reactions were also successful for preparing the halide compounds. The products are isolated as volatile liquids ($C_5H_5BeCH_3$) or solids (halide compounds). The compounds are stable with respect to redistribution and highly sensitive to air or moisture. As beryllium alkyls are toxic, this series of volatile compounds should be handled with extreme care. Molecular weight determinations (cryoscopic) confirm that the compounds are monomeric in benzene solution. Infrared data show that there is no significant structural difference between the species in solution and in the vapor phase.

The vapor-phase structures of $C_5H_5BeCH_3$,[14] C_5H_5BeCl,[15] C_5H_5BeBr,[16] and $C_5H_5BeBH_4$[17] have been determined by electron diffraction. The structure of C_5H_5BeCl was also determined by microwave spectroscopy and gave identical parameters.[18] In all cases the beryllium was found to lie on the fivefold symmetry axis of the cyclopentadienyl ring about 1.48 Å from the ring center. The Be–Cl bond distance in C_5H_5BeCl (1.837 ± 0.006 Å) was found to be significantly longer than in free, monomeric $BeCl_2$ (1.75 ± 0.002 Å).[19] The bonds in $BeCl_2$ are shortened due to considerable dative bonding between beryllium and chloride. Drew and Haaland suggested that such interaction is absent in C_5H_5BeCl because a six-electron covalent interaction is present between beryllium and the cyclopentadienyl ring. The bonding scheme proposed is as follows. The Be atom is sp hybridized, bonding with hybrid orbitals to the chlorine and to the a_1 π molecular orbitals of the ring. The two unhybridized 2p orbitals on the beryllium overlap with the filled e_1 π orbitals on the ring forming two degenerate bonding molecular orbitals. The beryllium atom is therefore surrounded by an octet of electrons. Since the compound is not "electron deficient", there is relatively little tendency to form oligomers or to coordinate with solvents. This view receives some support from recent molecular orbital calculations on dicyclopentadienylberyllium[20] which show that bonding between Be and the nearer cyclopentadienyl ring is effected primarily through molecular orbitals formed from the e_1 π orbitals and the $2p_x$ and $2p_y$ atomic orbitals on the metal. The spectroscopic data presented in this paper fully support the model of Drew and Haaland involving a covalent metal–ring triple bond.

Experimental Section

Instruments. Infrared spectra were recorded on a Perkin-Elmer Model 621 spectrophotometer. Three gas cells were utilized: a 10-cm cell fitted with KBr windows, a 10-cm cell with BaF_2 windows, and a 6-cm cell with polyethylene-coated KBr windows. A heating jacket was employed to obtain vapor-phase spectra for less volatile compounds. Samples were vapor transferred directly into the cells.

NMR spectra were recorded from a Varian Associates HA-100 spectrometer. Beryllium resonance spectra were obtained using a Varian V-4311 radiofrequency unit at 14.05 MHz with a field of 23.5 kG. Beryllium chemical shifts were measured by replacing an audio-modulated reference sample of aqueous beryllium nitrate without interruption of the field sweep. All sample tubes were degassed and torch sealed on a vacuum manifold.

Mass spectra were obtained from a Varian "MAT" Model CH-5. Compounds were vapor transferred from storage vessels into the instrument through a direct probe. The inlet system was cooled to 70 °C to help prevent thermal decomposition of the samples.

ESR spectra were recorded on a Varian Associates E-3 spectrometer.

Molecular weights were determined cryoscopically in benzene solutions. The concentrations of solutions were determined by beryllium analysis. All measurements were made under a nitrogen atmosphere.

Materials. Benzene, toluene, *p*-xylene, tetrahydrofuran, and cyclohexane were Reagent Grade and dried by distillation from sodium metal. Dimethylmercury was purchased from Eastman Organic Chemicals. Beryllium metal (200 mesh) was obtained from the Bush Beryllium Co. Dicyclopentadiene was obtained from Eastman Organic Chemicals and thermally dedimerized prior to use. Beryllium iodide was purchased from K&K, Inc. Beryllium fluoride was obtained from Alfa Inorganics, Inc. Beryllium chloride was prepared by the reaction between beryllium and chlorine gas in hot-tube reaction. Beryllium bromide was generously supplied by Dr. Richard Andersen and Professor G. E. Coates at the University of Wyoming.

Preparation of Compounds. All preparation and handling of organoberyllium compounds were carried out in a drybox or on a vacuum manifold.

Dimethylberyllium, $(CH_3)_2Be$, was prepared by a published method[21] from dimethylmercury and beryllium metal in a sealed-tube reaction. The compound was freshly sublimed at 90 °C under vacuum prior to further reaction.

Dicyclopentadienylberyllium, $(C_5H_5)_2Be$, was prepared by a published method[22] from the reaction of sodium cyclopentadienide with $BeCl_2$ in THF solution. The product was sublimed at 40 °C under vacuum as colorless plates (mp 59 °C) prior to further reaction.

Cyclopentadienyl(methyl)beryllium, $C_5H_5BeCH_3$ (in Benzene Solution). To one arm of a double Schlenk tube was added 0.50 g (13 mmol) of dimethylberyllium and a magnetic stirring bar. In the other arm, 0.38 g (2.7 mmol) of $(C_5H_5)_2Be$ was dissolved in 25 mL of benzene. The benzene solution was filtered through the center frit onto the dimethylberyllium and the mixture stirred for 5 min. The product (dissolved in benzene) was then refiltered through the frit leaving the insoluble, excess dimethylberyllium behind. The high volatility of the product prevented separation from the solvent but the presence of $C_5H_5BeCH_3$ was confirmed by IR and NMR spectra of the solution.

Cyclopentadienyl(methyl)beryllium, $C_5H_5BeCH_3$ (Prepared without Solvent). The reaction vessel used in all solid-phase reactions consisted of a 30-cm^3 reaction chamber connected through a Pyrex V-4 stopcock with a 14/35 inner joint for attachment to the vacuum manifold. The chamber had a side arm and cap with 14/35 fittings to allow admittance of the reactants.

Through the side arm of the reaction vessel were added 0.20 g (5 mmol) of freshly sublimed dimethylberyllium and 0.20 g (1.4 mmol) of freshly sublimed $(C_5H_5)_2Be$. The system was quickly closed and removed from the glovebox. Warming the reaction mixture in a 50 °C bath caused the solid components to melt into a colorless liquid. The vessel was attached to the vacuum manifold, frozen with liquid nitrogen, and evacuated. Upon warming, the product, $C_5H_5BeCH_3$, was vapor transferred into a storage vessel. The less volatile, excess dimethylberyllium remained behind. $C_5H_5BeCH_3$ melts at −34 to −36 °C from long colorless needles to a clear liquid. The measured vapor pressure at 27 °C was 24 Torr. The molecular weight determined cryoscopically in benzene was 92 ± 5 (theoretical for monomer 89).

Cyclopentadienylberyllium Chloride, C_5H_5BeCl. The reaction vessel described above was charged with 0.10 g (0.72 mmol) of $(C_5H_5)_2Be$ and 0.20 g (2.5 mmol) of anhydrous $BeCl_2$. An immediate reaction was noticed by formation of a clear liquid. The product was vapor transferred from excess $BeCl_2$ into a storage vessel. Cyclopentadienylberyllium chloride forms colorless needles melting without decomposition at 43–44 °C. The measured vapor pressure at 27 °C was 1.0 Torr. The molecular weight determined cryoscopically in benzene was 105 ± 7 (theoretical for monomer 109.6).

Table I. Comparison of Proton Chemical Shifts of Cyclopentadienylberyllium Complexes

Species	Solvent	τ	
		C_5H_5	CH_3
$C_5H_5BeCH_3$	Cyclohexane	4.11	11.74
	Benzene	4.15	11.20
	Toluene	4.18	11.18
C_5H_5BeCl	Benzene	4.12	
C_5H_5BeBr	Benzene	4.14	
C_5H_5BeI	Benzene	4.15	

Table II. Chemical Shifts from Variable-Temperature NMR Study of Cyclopentadienyl(methyl)beryllium in Toluene Solution

Temp (°C)	Chem shift, τ	
	C_5H_5 protons	CH_3 protons
+23	4.18	11.22
−40	4.33	11.02
−80	4.41	10.85

Cyclopentadienylberyllium Bromide, C_5H_5BeBr, and Cyclopentadienylberyllium Iodide, C_5H_5BeI. These compounds were prepared in the same manner as C_5H_5BeCl. The bromide analogue forms as small colorless needles which melt without decomposition at 33–35 °C. The molecular weight determined cryoscopically in benzene was 154 ± 10 (theoretical for monomer 154). The iodide complex melts without decomposition from small colorless needles at 32–33 °C.

Attempted Preparation of Cyclopentadienylberyllium Fluoride, C_5H_5BeF. No reaction was observed between $(C_5H_5)_2Be$ and BeF_2. The vapor-phase infrared spectrum of the mixture contained cyclopentadiene bands.

Attempted Preparation of Methylberyllium Chloride, CH_3BeCl. No reaction occurred when equimolar amounts of dimethylberyllium and $BeCl_2$ were heated together at 140 °C for 1 h.

Results and Discussion

NMR Spectra. Proton chemical shift data for cyclopentadienyl(methyl)beryllium and the halide complexes are given in Table I. The spectra of $C_5H_5BeCH_3$ consist of two sharp singlets with the expected area ratio of 5:3. The methyl resonance is somewhat influenced by solvent being at τ 11.74 in cyclohexane and at τ 11.20 and 11.18 in benzene and toluene. The ring proton signals in the halide complexes all appear as sharp singlets. Results of a low-temperature study of the methyl complex are recorded in Table II. At lower temperatures the ring proton signal shifts to slightly higher field while a slight shift downfield is observed for the methyl signal. No splitting of of the ring resonance was observed at −80 °C. Dicyclopentadienylberyllium is reported to complex with aromatic solvents forming paramagnetic, dimeric species containing two molecules of $(C_5H_5)_2Be$ per molecule of benzene or toluene.[22] Clearly, $C_5H_5BeCH_3$ does not form analogous complexes with aromatic solvents. Molecular weight determinations show the complex to be monomeric in benzene and the NMR spectra show no evidence for complexed solvent. In addition, no ESR signals were obtained for benzene or toluene solutions of the complex at temperatures as low as −150 °C.

Beryllium-9 resonance chemical shifts for the complexes are given in Table III. Two measurements were recorded for each sample and the chemical shifts were found to be reproducible to 0.01 ppm. All signals appear as sharp singlets ranging from a half-height width of 3 Hz for C_5H_5BeCl to 10 Hz for $C_5H_5BeCH_3$. The great shielding of the beryllium nucleus observed for compounds containing the cyclopentadienyl ring as compared with other beryllium complexes can be attributed to strong ring current effects.[23] The chemical shift observed

Table III. Beryllium-9 Chemical Shifts for Cyclopentadienylberyllium Compounds

Species	Solvent	^{9}Be chem shift,^{a} ppm	Width at half-peak height, Hz
$C_5H_5BeCH_3$	Cyclohexane	+20.1	7
	Benzene	+20.6	10
	Toluene	+20.5	9
C_5H_5BeCl	Benzene	+18.8	3
C_5H_5BeBr	Benzene	+19.5	4
$(C_5H_5)_2Be^b$	Toluene	+18.5	
	Methylcyclohexane	+18.3	

^{a} With reference to $Be(H_2O)_4^{2+}$. ^{b} Value taken from ref 22.

Table IV. Infrared Band Assignments for Cyclopentadienyl(methyl)beryllium, $C_5H_5BeCH_3$

Freq, cm^{-1}		
Vapor^a	Soln^b	Assignment
3123 w	3114 w	A_1 CH str (ring)
2938 m	2920 s	E_1 CH asym str
2868 m	2847 m	A_1 CH sym str
2426 w		1215 + 1215 = 2430
2222 w		1215 + 1014 = 2229
2082 w		
1809 m		1014 + 789 = 1803
1724 m	1725 w	
1608 w	1591 w	
1445 w		E_1 CC str (ring)
1215 vs (PQR)	1193 s	A_1 CH_3 sym def
1127 m (PQR)	1115 m	A_1 CC str (ring)
1080 m, sh		A_1 BeC str (methyl)
1014 vs	995 vs	E_1 CH in-plane bend (ring)
828 s (PQR)	820 s	E_1 CH out-of-plane bend (ring)
789 s (PQR)	780 s	A_1 CH out-of-plane bend (ring)
684 m	727 s	E_1 CH_3 rock

^{a} The spectrum was recorded with a 10-cm cell fitted with KBr windows at 25 °C. ^{b} The spectrum was recorded on a benzene solution as a thin film between KBr plates. Bands due to the solvent are not included.

for $(C_5H_5)_2Be$ is very close to the complexes containing only one cyclopentadienyl ring and seems to indicate that in $(C_5H_5)_2Be$ the beryllium atom is influenced by only one of the rings (the closer one).

Infrared Spectra. A detailed infrared and Raman analysis for liquid and solid C_5H_5BeCl, $C_5H_5BeBH_4$, and $C_5H_5BeBD_4$ has been recently published.[27] The results clearly show that the fundamental frequencies pertaining to the cyclopentadienyl ring must be assigned with local C_{5v} symmetry for the metal-ring species (as apposed to D_{5h} symmetry that would be consistent with an electrostatic ring).

The spectrum of cyclopentadienyl(methyl)beryllium was recorded in the vapor phase and as a thin film in benzene solution between KBr plates. Assignments (Table IV) are made by analogy with the spectra of $(CH_3)_2Be$,[24] CH_3BeBH_4,[25] and $(C_5H_5)_2Be$[13] and the infrared analysis mentioned above. The ring fundamentals are assigned under C_{5v} symmetry and the methylberyllium fundamentals under local C_{3v} symmetry. The beryllium–methyl carbon stretch is tentatively assigned to a weak absorption at 1080 cm^{-1} (1081 cm^{-1} in Me_2Be; 1108 cm^{-1} in $MeBeBH_4$).

The fundamental infrared frequency assignments for gaseous C_5H_5BeCl and C_5H_5BeBr are given in Table V. The corresponding absorptions for solid C_5H_5BeCl are presented for comparison. The assignments are based on C_{5v} symmetry for the molecules. The results confirm that the bonding interactions and structures of the vapor and solid are identical. The Be–Cl stretching frequency is assigned to a weak shoulder observed at 1070 cm^{-1}. The terminal Be–Cl stretch in monomeric $BeCl_2$ is observed at 1113 cm^{-1}.[26] The vapor-phase spectrum of C_5H_5BeBr contains only three fundamentals assignable to the ring. The absence of an absorption in the range 1126–1097 cm^{-1} may reflect a higher degree of ionic interaction between beryllium and the ring. While the band assigned to the Be–Br stretch, 970 cm^{-1}, is at lower frequency than observed in monomeric $BeBr_2$, 1010 cm^{-1},[28] the Be–Br distance in C_5H_5BeBr[16] (1.943 ± 0.015 Å) is not significantly greater than that reported for monomeric $BeBr_2$ (1.92 ± 0.02 Å).[29] Because of the difference in size of the pertinent p orbitals in $BeCl_2$ and $BeBr_2$ less dative π bonding in the bromide compounds may be expected.

Table V. Fundamental Vibrational Frequencies for C_5H_5BeCl and and C_5H_5BeBr in the Vapor Phase (cm^{-1})

Freq, cm^{-1}			
$C_5H_5BeCl^a$ (solid)	$C_5H_5BeCl^b$ (vapor)	$C_5H_5BeBr^b$ (vapor)	Assignment
3120	3091 w	3097 w	A_1 CH str
3112			E_1 CH str
1427	1437 w		E_1 CC str
1126	1124 m (PQR)		A_1 CC str
1018	998 vs (PQR)	996 s (PQR)	E_1 CH in-plane bend
866	870 s	901 s	E_1 CH out-of-plane bend
	1070 w		A_1 Be–Cl str
		970 m	A_1 Be–Br str

^{a} Values taken from ref 27. ^{b} Spectra recorded at 70 °C.

Table VI. Mass Spectra of Cyclopentadienyl(methyl)beryllium^a

12 eV		20 eV		
m/e	% base	*m/e*	% base	Assignment
90	13.34	90	4.44	89 + 1
89	100.00	89	66.60	$C_5H_5BeCH_3^{+\cdot}$
		75	5.55	74 + 1
74	33.35	74	100.00	$C_5H_5Be^+$
66	60.03	66	17.76	$C_5H_6^{+\cdot}$
		65	4.44	$C_5H_5^+$
		16	7.77	$CH_4^{+\cdot}$
		15	4.40	CH_3^+

^{a} Source temperature 90 °C; sample pressure 3 × 10^{-4} Torr.

The infrared spectrum of gaseous cyclopentadienylberyllium iodide could not be obtained using KBr optics because of rapid reaction with the cell plates. The spectrum obtained with BaF_2 cell plates contained two bands assignable to the cyclopentadienyl ring. A weak band at 3090 cm^{-1} is the C–H stretch. A medium-intensity band at 992 cm^{-1} is assigned to the parallel C–H deformation. A strong absorption noted at 890 cm^{-1} is assigned to cyclopentadiene decomposition.

Mass Spectra. The mass spectral data for $C_5H_5BeCH_3$ at ionizing voltages of 12 and 20 eV are presented in Table VI. The spectra indicate the presence of small amounts of cyclopentadiene and methane that may have formed from thermal decomposition caused by the relatively high source temperature of 90 °C. In the 12-eV spectrum the parent ion is the base peak. Fragmentation of the parent to a methyl radical and a cyclopentadienylberyllium cation, $C_5H_5Be^+$ (*m/e* 74), is observed. At 20 eV the $C_5H_5Be^+$ species accounts for the base peak. It appears that this species is quite stable which would be consistent with a strong covalent interaction as proposed between the metal and ring. In neither spectrum is a methylberyllium cation (*m/e* 24) observed which would result from cleavage of the ring from the parent ion. The spectrum of the complex was also recorded at 70 eV, but the data were complicated and a comprehensive analysis was not undertaken. The spectrum is dominated by fragmentation of the cyclopentadienyl ring. Two significant metastable peaks are observed; a relatively sharp peak at *m/e* 64 indicates

Table VII. Mass Spectra of Cyclopentadienylberyllium Bromide[a]

20 eV		70 eV		
m/e	% base	*m/e*	% base	Assignment
155	42.0	155	10.8	$C_5H_5BeBr^{+\cdot}$(^{81}Br)
153	42.6	153	11.1	$C_5H_5BeBr^{+\cdot}$(^{79}Br)
90	6.8	90	66.0	$BeBr^+$ (^{81}Br)
88	7.0	88	67.7	$BeBr^+$ (^{79}Br)
		81	6.0	$^{81}Br^+$
		79	6.0	$^{79}Br^+$
74	100.0	74	65.0	$C_5H_5Be^+$
		65	35.0	$C_5H_5^+$
		39	100.0	$C_3H_3^+$
		38	62.7	$C_3H_2^+$

[a] Source temperature 160 °C; sample pressure 3 × 10^{-4} Torr.

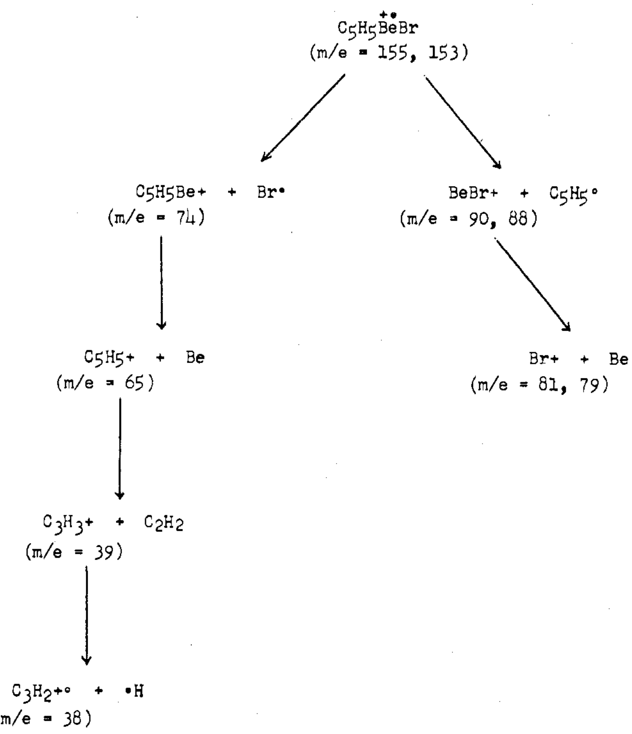

Figure 1. Fragmentation pathways for cyclopentadienylberyllium bromide at 70 eV.

formation of the cyclopentadienyl cation (*m/e* 65) from the cyclopentadienyl radical cation (*m/e* 66). This indicates that the $C_5H_5^+$ fragment does not form from the parent ion. The other metastable peak at *m/e* 61.5 results from primary fragmentation of the parent ion where a methyl radical is cleaved. Thus $C_5H_5Be^+$ forms directly from the parent ion.

Mass spectra of C_5H_5BeCl were recorded at 12, 20, and 70 eV. The spectra reflect a large amount of cyclopentadiene contamination. The source temperature of 160 °C was probably too high to prevent some thermal decomposition. At 12 eV no fragmentation of the parent ion is observed. The 20-eV spectrum has the *m/e* 74 peak ($C_5H_5Be^+$) but no peaks for the $BeCl^+$ species. The formation of beryllium chloride cations (*m/e* 44, 46) is observed in the spectrum recorded at 70 eV.

The spectra of C_5H_5BeBr recorded at ionizing voltages of 20 and 70 eV are presented in Table VII. The spectra are superior to those of $C_5H_5BeCH_3$ and C_5H_5BeCl as no cyclopentadiene impurity or decomposition products contaminate the sample. All fragments containing bromide appear as two peaks of nearly equal intensity and 2 mass units apart due to the natural isotopic abundance of bromine (50.57% ^{79}Br and 49.43% ^{81}Br). The 20-eV spectrum contains strong parent ions (*m/e* 155, 153). Loss of bromine radicals from the parent ions forming $C_5H_5Be^+$ (*m/e* 74) account for the base peak. To a lesser extent (7%) cleavage of a cyclopentadienyl radical from the parent forming the beryllium bromide cations (*m/e* 90, 88) is observed. At 70 eV the parent ions are losing bromine radicals with about half the frequency as cyclopentadienyl radicals. Further fragmentation of the beryllium bromide cations to Br^+ and beryllium atoms is observed. The fragmentation pathways for C_5H_5BeBr are represented in Figure 1.

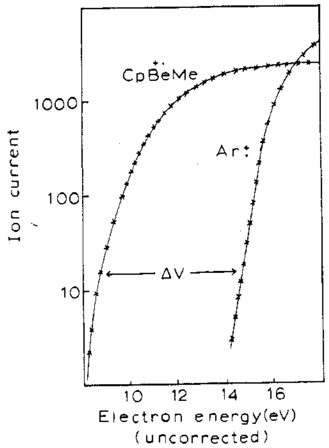

Figure 2. Ion efficiency curves for $C_5H_5BeCH_3^{+\cdot}$ and Ar^+ (semilog scale).

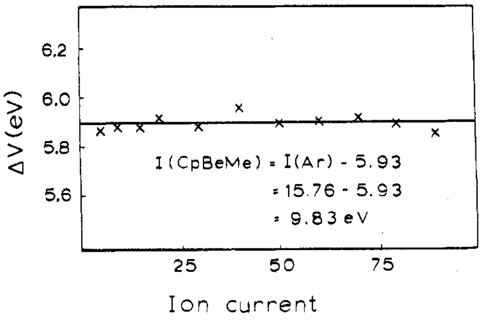

Figure 3. Ionization potential of $C_5H_5BeCH_3$.

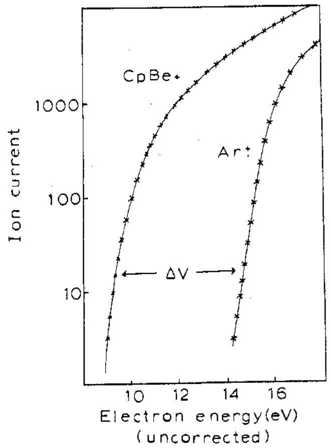

Figure 4. Ion efficiency curves for $C_5H_5Be^+$ and Ar^+ (semilog scale).

Appearance Potentials. The strength of the beryllium–methyl carbon bond in the parent ion of the complex $C_5H_5BeCH_3$ was determined from appearance potential measurements utilizing the Warren method.[30] The ion efficiency curves for the parent ion and argon reference are shown in Figure 2. The appearance potential of the parent ion is a direct measure of the vertical ionization potential of the complex. Since the $C_5H_5Be^+$ species is formed directly

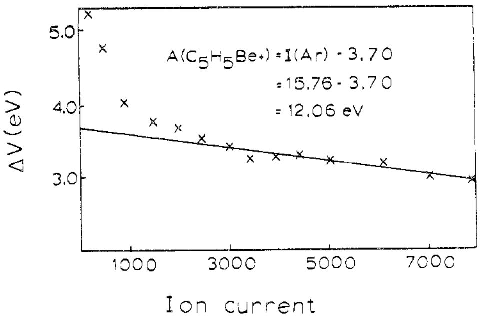

Figure 5. Appearance potential for $C_5H_5Be^+$.

from the parent ion, the dissociation energy of the Be–C bond in the parent ion can be determined using eq 2. The ionization potential of $C_5H_5BeCH_3$ (Figure 3) is 9.83 eV. The appearance potential for $C_5H_5Be^+$ (Figures 4 and 5) is 12.06 eV. The calculated bond dissociation energy is 51 kcal/mol. The observed tailing in Figure 5 suggests that the dissociation process occurs with excess kinetic energy and the derived bond energy should be regarded as the upper limit. The bond energies (Be–C) in a series of dialkylberyllium monomers have been determined in an analogous manner.[31] For comparison the Be–C bond energy in dimethylberyllium is reported to be 46.1 kcal/mol.

$$DE(C_5H_5Be\cdot\cdot\cdot CH_3) = AP(C_5H_5Be^+) - IP(C_5H_5BeCH_3) \qquad (2)$$

Acknowledgment. This research was supported by the National Science Foundation under Grant No. GP-8595. We thank Dr. David Nelson at the University of Wyoming for help in obtaining the mass spectral data.

Registry No. $C_5H_5BeCH_3$, 36351-95-8; C_5H_5BeCl, 36346-97-1; C_5H_5BeBr, 52140-35-9; C_5H_5BeI, 62571-44-2; $(CH_3)_2Be$, 506-63-8; $(C_5H_5)_2Be$, 12083-43-1.

References and Notes

(1) To whom correspondence should be addressed at the Department of Physical Science, Rhode Island College, Providence, R.I. 02908.
(2) G. F. Reynolds and S. R. Daniel, *Inorg. Chem.*, **6**, 480 (1967).
(3) M. D. Rausch and J. R. Van Wazer, *Inorg. Chem.*, **3**, 761 (1964).
(4) H. O. House, R. A. Latham, and G. M. Whitesides, *J. Org. Chem.*, **32**, 2481 (1967).
(5) G. E. Parris and E. C. Ashby, *J. Organomet. Chem.*, **72**, 1 (1974).
(6) J. R. Sanders, Jr., E. C. Ashby, and J. H. Carter II, *J. Am. Chem. Soc.*, **90**, 6385 (1968).
(7) N. A. Bell, *J. Organomet. Chem.*, **13**, 513 (1968).
(8) E. L. Head, C. F. Holley, and S. W. Pabideau, *J. Am. Chem. Soc.*, **79**, 3687 (1957).
(9) G. E. Coates and P. D. Roberts, *J. Chem. Soc. A*, 2651 (1968).
(10) E. O. Fischer and S. Schreiner, *Chem. Ber.*, **92**, 938 (1959).
(11) D. A. Drew and A. Haaland, *Acta Crystallogr., Sect. B*, **28**, 3671 (1972).
(12) C. H. Wong, T. Y. Lee, K. J. Chao, and S. Lee, *Acta Crystallogr., Sect. B*, **28**, 1668 (1972).
(13) G. B. McVicker and G. L. Morgan, *Spectrochim. Acta, Part A*, **26a**, 23 (1970).
(14) D. A. Drew and A. Haaland, *Acta Chem. Scand.*, **26**, 3079 (1972).
(15) D. A. Drew and A. Haaland, *Acta Chem. Scand.*, **26**, 3351 (1972).
(16) A. Haaland and D. P. Novak, *Acta Chem. Scand., Ser. A*, **28**, 3 (1974).
(17) D. A. Drew, G. Gundersen, and A. Haaland, *Acta Chem. Scand.*, **26**, 2147 (1972).
(18) A. Bjorseth, D. A. Drew, K. M. Marstokk, and H. Mollendal, *J. Mol. Struct.*, 13 (1972).
(19) P. A. Akishin, V. P. Spiridonov, and G. A. Sabolov, *Dokl. Akad. Nauk SSSR*, **118**, 1334 (1958).
(20) O. Y. Lopatko, N. M. Klimenko, and M. E. Dyatkina, *J. Struct. Chem.* (*Engl. Transl.*), **13**, 1044 (1972).
(21) H. Gilman and F. Schulze, *J. Am. Chem. Soc.*, **49**, 2904 (1927).
(22) G. L. Morgan and G. B. McVicker, *J. Am. Chem. Soc.*, **90**, 2789 (1968).
(23) R. A. Kovar and G. L. Morgan, *J. Am. Chem. Soc.*, **92**, 5067 (1970).
(24) R. A. Kovar and G. L. Morgan, *Inorg. Chem.*, **8**, 1099 (1969).
(25) T. H. Cook and G. L. Morgan, *J. Am. Chem. Soc.*, **92**, 6487 (1970).
(26) A. Buchler and W. Klemperer, *J. Chem. Phys.*, **29**, 121 (1958).
(27) D. A. Coe, J. W. Nibler, T. H. Cook, D. Drew, and G. L. Morgan, *J. Chem. Phys.*, **63**, 4842 (1975).
(28) A. Snelson, *J. Phys. Chem.*, **72**, 250 (1968).
(29) P. A. Akishin and V. P. Spiridinov, *Kristallografiya*, **2**, 475 (1957).
(30) J. W. Warren, *Nature (London)*, **165**, 810 (1950).
(31) D. B. Chambers, G. E. Coates, and F. Glockling, *J. Chem. Soc. A*, 741 (1970).

Contribution from the Departments of Chemistry and Physics,
Kansas State University, Manhattan, Kansas 66506

Magnetic Isomers of Iron(II). Bis(*C*-cyanotrihydroborate)bis(phenanthroline)iron—a Spin Triplet[1]

KEITH F. PURCELL,* SAM MINGJAVE YEH, and JOHN S. ECK

Received November 23, 1976 AIC60850X

The synthesis of an unusual six-coordinated, spin triplet ($S = 1$) ferrous complex, $Fe(phen)_2(NCBH_3)_2$, with cis geometry is described. This complex is characterized by its magnetic moment and infrared, visible-region, and Mössbauer spectra. On the basis of these data and the angular overlap model of metal–ligand bonding, $^-NCBH_3$ is characterized as a ligand possessing moderate σ- and π-donor characteristics toward $Fe(phen)_2^{2+}$. How a proper balance of σ- and π-donor properties of $-NCBH_3$ and phen yields the spin-triplet state of the ferrous complex is discussed. Consideration of the CN stretching frequency data for the isomeric pairs of $Fe(phen)_2(NCBH_3)_2$ and $Fe(phen)_2(CNBH_3)_2$ and other bridged cyano species raises interesting questions about the effect of double coordination of cyanide on the CN σ bonding. Finally, thermal stability studies of the Fe–CN–BH_3 and Fe–NC–BH_3 linkages eliminate the possibility of isomerization by a facile CN flip mechanism within the Fe and B cage and suggest that $(phen)_2Fe(NCBH_3)_2$ is the thermodynamically favored isomer.

Since our initial suggestion[2a] that $NCBH_3^-$ possesses a significant degree of coordinating ability there have been several reports of such complexes.[3] Most of the latter have exhibited N-coordination but in the case of $[Cu(PPh_3)_2(NCBH_3)]_2$ coordination of Cu by N *and* H of $NCBH_3^-$ has been documented.[3d,e] Furthermore, different modes of synthesis affect the structure of at least one complex $[Cu(PPh_3)_3(NCBH_3)]$, for both N- and H-bound forms are claimed.[3c,d] Other examples of H-bound $NCBH_3^-$ have also been reported.[3c]

While we had a variety of reasons to attempt synthesis of $Fe(phen)_2(NCBH_3)_2$, two of the more important ones have been (i) a desire to prepare the isomer of $Fe(phen)_2(CNBH_3)_2$[4] (with the intent to investigate the interconversion of these bridged cyano species) and (ii) the promise that $Fe(phen)_2(NCBH_3)_2$ might have unusual magnetic properties. This latter prediction derives from the unusual magnetic properties[5] of $Fe(phen)_2(NCS)_2$ ($S = 2$ above 173 K, $S = 0$ below 170 K). The only examples, of which we are aware, of two molecular linkage isomers of bridging cyanide are $(H_3N)_5Co(CN,NC)Co(CN)_5$[6] and $H(Et_3P)_2Pt(CN,NC)BPh_3$;[7] the latter was reported as this work neared completion.

The subjects of this report are the synthesis of $Fe(phen)_2(NCBH_3)_2$, its electronic structure, the characterization