Recent Developments in the Chemistry of Beryllocenes

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Synthetic studies on substituted beryllocenes have provided new representatives of this family of compounds. Knowledge of their structures gives a better understanding of the long-standing problem of the structure of the parent beryllocene, $Be(C_5H_5)_2$. Theoretical calculations offer a clear picture of their bonding properties, while spectroscopic and reactivity investigations have clarified their dynamic behaviour. Beryllocenes of the type $BeCp'_2$ (Cp′ = methyl-substituted cyclopentadienyl group) and half-sandwich cyclopentadienylberyllium compounds are considered.

Introduction

The chemistry of metallocenes started in the early 1950s with the preparation of ferrocene and the recognition of its correct structural and bonding properties.[1] The first main-group metallocenes – the tin and lead compounds $M(C_5H_5)_2$ – were synthesised shortly afterwards.[2] In 1959, $[Be(C_5H_5)_2]$, the lightest member of the alkaline-earth metallocenes and of the general bis(metallocene) series of compounds MCp'_2, was obtained as a volatile, sublimable solid from the reaction of $BeCl_2$ and NaC_5H_5.[3] Over the years, introduction of the pentamethylcyclopentadienyl and other substituted cyclopentadienyl ligands (from now on generally represented by Cp′), including those with bulky substituents, has converted the metallocenes of the alkaline-earth elements into an attractive family of compounds that are characterised by a rich variety of structures.[4]

Beryllocene and some substituted beryllocenes possess a slipped-sandwich structure, whereas the magnesocenes feature parallel (i.e. ferrocene-like) sandwich arrangements.[4] Calcocene adopts an unexpected nonparallel polymeric structure but $[Ca(C_5Me_5)_2]$ is monomeric, although also with nonparallel rings, and this is the structure found in

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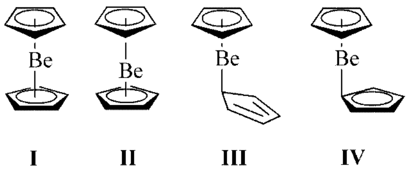
most MCp′$_2$ compounds of the heavier group 2 elements Ca, Sr and Ba.[4] Interestingly, this structural diversity appears to emerge from a simple, predominantly electrostatic, $M^{2+}\cdots 2Cp'^{-}$ bonding model. Theory predicts[5] that in the unsubstituted metallocenes of Mg to Ba [M(C$_5$H$_5$)$_2$] electrostatic forces account for approximately 70–85% of the total interaction energy. As expected, [Be(C$_5$H$_5$)$_2$] is more covalent,[5] and replacement of C$_5$H$_5$ by C$_5$Me$_5$ (viz. in [Be(C$_5$Me$_5$)$_2$]) results in further reduction of the ionicity by almost 10%. Numerous quantum chemical calculations on main-group metallocenes have been published in recent years, and the theoretical knowledge gained from these studies has been reviewed recently by Kwon and McKee, who concluded that "there is not enough data from high-level theoretical calculations to have a quantitative understanding of the factors involving covalent or ionic bonding between the Cp ligand and the main-group element".[6]

As already mentioned, the use of Cp′ ligands with different substituents and degrees of substitution has permitted the synthesis and characterisation of many MCp′$_2$ derivatives of the alkaline-earth elements. The chemistry of these complexes has been compiled in several review articles,[4] usually as part of larger overviews of main-group organometallic compounds. In this Microreview we concentrate on beryllocenes. We revise the longstanding problem of the structure of the parent [Be(C$_5$H$_5$)$_2$] and focus on the latest advances in this field. In particular, we discuss the structure and bonding properties of the recently reported beryllocenes with C$_5$Me$_5$ and C$_5$Me$_4$H rings. Chemical, spectroscopic (NMR) and theoretical studies have provided useful information on their dynamic behaviour. Both bis(cyclopentadienyl) and half-sandwich mono(cyclopentadienyl) beryllium derivatives are examined.

Bis(cyclopentadienyl)beryllium [Be(C$_5$H$_5$)$_2$] (1)

Since the preparation of beryllocene by Fisher and Hofmann in 1959,[3] its structure has provoked a long and controversial debate. Structures **I**–**IV** are some of the proposed models.



The symmetrical ferrocene-like structure **I** was ruled out because the complex has a permanent dipolar moment in solution[3] (2.24 D in cyclohexane at 25 °C). The first gas-phase electron diffraction study carried out in 1964[7] suggested a non-symmetrical structure **II**, with the Be atom unsymmetrically disposed between the two Cp rings,[8] while molecular orbital calculations[9] were in favour of a non-symmetrical structure of type **III**, in which there is an ionic η^5-Cp ring and a covalently bonded η^1-Cp ring.

Three X-ray studies were carried out between 1972 and 1984. The first, at –120 °C,[10] showed a slipped-sandwich structure **IV**, which was unprecedented at that time. The two Cp rings were found to be parallel and separated by 3.33 Å. The Be atom was disordered between two sites, being η^5-coordinated to one Cp ring (Be–Cp$_{centr}$ = 1.53 Å), and η^1-coordinated to the other, with a Be–C separation of 1.81(5) Å. This is longer than the Be–Me distance found in the complex [Be(η^5-C$_5$H$_5$)Me][11] (1.706 Å). The same authors carried out a second X-ray investigation, this time at room temperature, that showed similar results, but with the two Cp rings partially eclipsed.[12] A new electron diffraction study provided data compatible with the slipped-sandwich structure.[13]

The third X-ray diffraction determination was carried out in 1984 at –145 °C[14] and also showed a slipped-sandwich structure with disorder at the beryllium atom that alternates its position between two points separated by 1.303 Å. The Be–C–C angles between the metal and the η^1-ring were close to 90° and an important electronic delocalisation of the π-system of this ring was ascertained, with the negative charge being only partially localised on the carbon atom bonded to beryllium. Very recently, a new X-ray crystallographic analysis of [Be(C$_5$H$_5$)$_2$] was performed at 20 °C and at –100 °C. At the lower temperature the structure is of the reported η^5/η^1 type but at 20 °C it appears closer to η^5/η^2 coordination.[15]

The slipped-sandwich structure **IV** explains the microwave spectroscopic data of **1**.[16] Moreover, the IR spectrum of [Be(C$_5$H$_5$)$_2$] shows little variation between the solid, solution and vapour states.[17] Similarly, the Raman spectrum of solid beryllocene recorded between 160 and 25 °C, and of the liquid at 65 °C, shows no significant differences.[18] Hence, it is clear that the solid-state structure is maintained in all phases.

Adoption of a slipped-sandwich geometry by [Be(C$_5$H$_5$)$_2$] has been rationalised by Beattie and Nugent.[19] A variety of structures found for main-group metal cyclopentadienyls, ranging from the centrally bound ferrocene-type to peripherally bonded structures, were discussed. The energy of the M–C$_5$H$_5$ interaction can be considered as resulting from two effects, namely the strength of the M–C bond and the π-system delocalisation energy. The latter is a minimum for η^5-coordination whereas the η^1/σ binding mode provides the strongest M–C interaction. For an element like beryllium, which forms Be–C bonds of intermediate bond-heterolysis energy, neither of the two forces predominates and the compromise slipped-sandwich structure becomes the most favourable.[19]

Beryllocene is a highly fluxional molecule both in solution[20] and in the condensed phase,[15] according to ^{1}H, ^{9}Be and ^{13}C variable temperature NMR studies. The ^{1}H and the ^{13}C nuclei of the two C$_5$H$_5$ rings are magnetically equivalent down to –125 °C, which implies that their exchange is rapid even at these low temperatures. Molecular dynamics calculations[21] have identified two very facile rearrangements, namely a 1,5-sigmatropic shift of the Be(η^5-C$_5$H$_5$) unit around the periphery of the η^1-C$_5$H$_5$ ring and a "molecular inversion" process that interchanges the η^5 and η^1 ligands. The first is proposed to occur through an η^5/η^2

transition state, with an activation barrier of 5 kJ mol^{-1}, while for the second an activation energy of 8 kJ mol^{-1} associated with an η^3/η^3 transition state was calculated.[21] Very recently Hung, Macdonald and Schurko[15] have made an important contribution to our understanding of the solid-state structure and dynamics of different beryllocenes and have provided, among other relevant information, an experimentally determined value of 36.9 kJ mol^{-1} for the activation energy of the "molecular inversion" in $[Be(C_5H_5)_2]$ in the solid state.

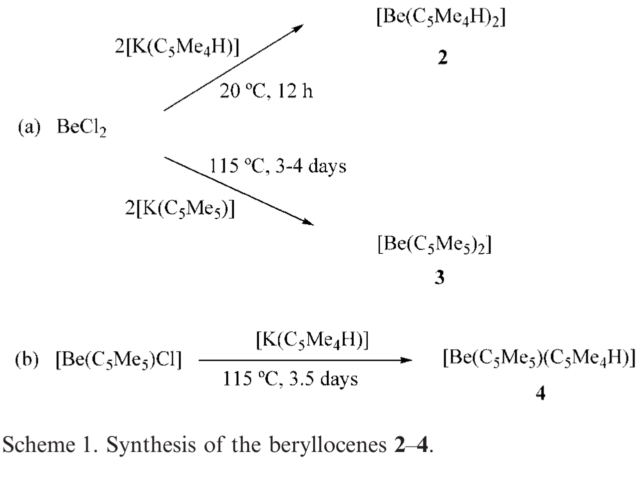
Numerous theoretical studies have attempted to explain the structure and other properties of $[Be(C_5H_5)_2]$.[21,22] Among the most recent ones, Rayón and Frenking found that at the BP86/6-31G(d) level the η^5/η^1 structure of C_s symmetry is a minimum on the potential energy surface, although with similar energy to the η^5/η^5 D_{5d} structure. The calculations indicate that the potential energy surface around the C_s/D_{5d} forms is very flat, in agreement with the fluxional structure of $[Be(C_5H_5)_2]$. Moreover, a significant covalent contribution (about 40%) to the bonding interaction was calculated. Similar structural conclusions were obtained by Budzelaar and co-workers, who found that the minimum energy structure for beryllocene has η^5 and η^1 rings[5c] that exchange via the η^3/η^3 structure with a barrier of around 7.5 kJ mol^{-1}.

Before closing the discussion on $[Be(C_5H_5)_2]$, two additional comments are appropriate. Firstly, dihydro-1*H*-azabororyl (Ab) species of composition $[Be(Ab)_2]$ and $[Be(C_5H_5)(Ab)]$ have been prepared as possible models for **1**, as this heterocyclic ligand is isostructural and isoelectronic with C_5H_5.[23] X-ray studies at –150 °C show that $[Be(Ab)_2]$ has η^5 and η^1 ligands that are not parallel but instead form an angle of 14.5°. Secondly, following the report from our group on the synthesis and structure of $[Zn_2(\eta^5\text{-}C_5Me_5)_2]$, an unprecedented dimetallocene that features a metal–metal bonded dizinc unit unsupported by bridging ligands,[24] a theoretical study of the analogous model compounds $[M_2(C_5H_5)_2]$ (M = Be, Mg, Ca) has been reported. The calculations predict that in diberyllocene, $[Be_2(C_5H_5)_2]$, each metal forms a covalent bond with the other, with a Be–Be distance of 2.06 Å, and a predominantly ionic linkage to the adjacent cyclopentadienyl ring.[25]

The Substituted Beryllocenes $[Be(C_5Me_4H)_2]$ (2), $[Be(C_5Me_5)_2]$ (3) and $[Be(C_5Me_5)(C_5Me_4H)]$ (4)

As already mentioned, in the last few years a large number of MCp'_2 compounds of the alkaline-earth metals from Mg to Ba have been prepared using Cp′ ligands with different substituents and degrees of substitution, and their solid-state structures have been determined by X-ray methods.[4] It was therefore surprising to find that, prior to our work, $[Be(C_5H_5)_2]$ was the only structurally characterised beryllocene, although the mixed-ring compound $[Be(C_5Me_5)(C_5H_5)]$ had been obtained when $[Be(\eta^5\text{-}C_5H_5)Cl]$ and $[Li(C_5Me_5)]$ were heated together in a melted mixture (60 °C).[26] It is possible that attempts to make other $[BeCp'_2]$ compounds may have been deterred by the general belief that the small Be^{2+} ion (ionic radius of 0.27 Å in coordination number 4; 0.45 Å estimated value for six-coordination environments)[27] could not accommodate two bulky cyclopentadienyl ligands. This would explain the formation of only the half-sandwich complex $[Be(\eta^5\text{-}C_5Me_5)Cl]$ from the treatment of $BeCl_2$ with C_5Me_5 transfer agents.[28] Nevertheless, the successful isolation of $[Be(C_5Me_5)_2]$ when $BeCl_2$ and $[K(C_5Me_5)]$ react in a diethyl ether/toluene mixture at 115 °C over 3.5 days (vide infra)[29] has revealed that $[Be(C_5Me_5)_2]$ is a stable complex and that it had not been generated before only because coordination of the second C_5Me_5 ring is a slow process with a high kinetic barrier. Recent attempts to synthesise $[Be(Cp^{3Si})_2]$, containing the bulky cyclopentadienyl Cp^{3Si} $[1,2,4\text{-}C_5H_2(SiMe_3)_3]$, under conditions similar to those used to prepare $[Be(C_5Me_5)_2]$, led only to decomposition products.[30] Since theory predicts an η^5/η^1 structure for the molecules of this compound, failure to generate it is probably due to kinetic difficulties and not to steric overcrowding.[30]

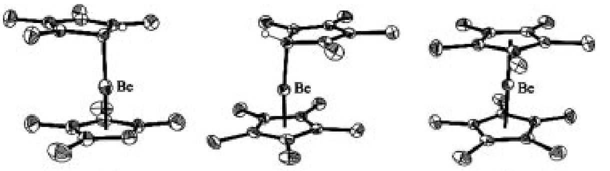
Octamethylberyllocene, $[Be(C_5Me_4H)_2]$ (**2**), and decamethylberyllocene, $[Be(C_5Me_5)_2]$ (**3**), have been synthesised by the reaction of $BeCl_2$ with $[K(C_5Me_4H)]$ and $[K(C_5Me_5)]$, respectively (Scheme 1, a). However, whereas compound **2** requires stirring at room temperature for about 12 h, the synthesis of **3** demands higher reaction temperatures (ca. 115 °C) and times (between 3 and 4 days) and even under these conditions the crude reaction mixture always contains small amounts of the half-sandwich complex $[Be(\eta^5\text{-}C_5Me_5)Cl]$.[29] Clearly, replacement of the chloride ligand by C_5Me_5 in the latter complex is difficult due to steric hindrance. In marked contrast, attempts to isolate the analogous $[Be(\eta^5\text{-}C_5Me_4H)Cl]$ derivative have proved fruitless – the use of stoichiometric amounts of $[K(C_5Me_4H)]$ leads only to $[Be(C_5Me_4H)_2]$ (**2**) and unreacted $BeCl_2$. In accordance with this, extended heating at high temperatures (Scheme 1, b) is also needed for the mixed-ring beryllocene $[Be(C_5Me_5)(C_5Me_4H)]$ (**4**), although the synthesis proceeds in high yield (isolated yields of crystalline **4** of around 70%). The three compounds are volatile, sublimable solids that are very soluble in common non-polar organic solvents. They are very reactive towards O_2 and H_2O and de-



Scheme 1. Synthesis of the beryllocenes **2**–**4**.

compose immediately upon exposure to air. Compounds **2** and **3** enlarge the beryllocenes series of complexes significantly, while the mixed-ring compound **4** finds precedent only in the related [Be(C_5Me_5)(C_5H_5)] derivative, formulated as [Be(η^5-C_5Me_5)(η^1-C_5H_5)] on the basis of solution IR and NMR spectroscopic studies.[26] Solid-state characterisation of this species by X-ray methods has not been reported.

Compounds **2**–**4** were characterised by X-ray crystallography at low temperatures (100–300 K); the corresponding ORTEP diagrams are given in Figure 1. Recently the structures of **2** and **3** have also been re-determined at low temperature, with similar results.[15]



2 **4** **3**

Figure 1. ORTEP perspectives of beryllocenes **2**, **3** and **4**.

Both [Be(C_5Me_4H)$_2$] (**2**) and [Be(C_5Me_5)(C_5Me_4H)] (**4**) exhibit η^5/η^1 geometries of the kind found for the parent beryllocene. Not unexpectedly, the structure of the mixed-ring beryllocene **4** consists of η^5-C_5Me_5 and η^1-C_5Me_4H binding. In the two compounds the η^1-C_5Me_4H ring bonds to the metal through the unique CH carbon, possibly to form a stronger Be–C bond.[29] The Be–CH bond lengths are identical within experimental error (1.77 Å) and compare well with the corresponding distance in [Be(C_5H_5)$_2$] [1.826(6) Å].[10,12,14] These Be–CH distances are in the middle of the range of Be–C bonds (1.70–1.85 Å).[29]

The coordination of the η^5-Cp′ ring is highly symmetrical, and for either compound the five Be–C separations are almost identical and cluster around 1.90 Å. Considering that the Be–C(η^5) bond lengths in [Be(C_5H_5)$_2$] have comparable values (average about 1.92 Å), it is evident that substitution of H by Me within the η^5-Cp′ ligand does not significantly alter the strength of the Be–C(η^5) bonds. The distances from beryllium to the η^5-C_5Me_5 ring centroids of **2** and **4** are also identical within experimental error (1.47 Å) and very similar to the corresponding separation in [Be(C_5H_5)$_2$] (1.50 Å).[10,12,14]

The Be–C(η^1)–ring plane angle in the two complexes **2** and **4** is close to 100–102°, far from the 125° value which would be expected for η^1-bonding to a tetrahedral ring carbon atom.[31] Similarly, the Be–C(η^1)–C angles to the adjacent carbon atoms are smaller (ca. 99°) than the ideal 109.5° value that would correspond to a tetrahedral geometry. Additionally, the η^5- and η^1-rings are almost planar and nearly parallel, the angles between the rings being 6.6(1)° and 4.9(1)° for **2** and **4**, respectively. In the three compounds **1**, **2** and **4** there is an alternation in the bond lengths within the η^1 ring which is characteristic of the slipped-sandwich structural type. As shown in Figure 2, the difference in the lengths of the $C_{\alpha\beta}$ and $C_{\beta\beta}$ bonds (C_α is the carbon atom adjacent to the beryllium-bound carbon) is only 0.06–0.07 Å. This reveals some diene character for the η^1 rings. Nevertheless, partial delocalisation of the π-system exists, as the differences in the C–C bonds are significantly smaller than in cyclopentadiene (0.12 Å) and in cyclopentadienyl rings bonded in the common η^1/σ fashion. Thus, in [B(η^5-C_5Me_5)(η^1-C_5Me_5)]$^+$[32] and [{Hg(η^1-C_5Me_4-$SiMe_2tBu$)Cl}$_4$][33] the C–C bonds are dissimilar by about 0.14 Å.

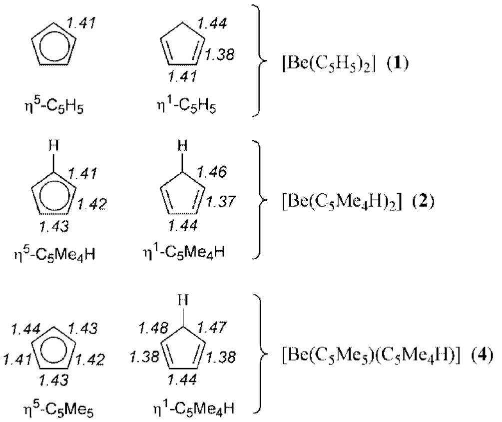


Figure 2. Lengths [Å] of the $C_{\beta\beta}$ and $C_{\alpha\beta}$ bonds in the Cp′ rings of **1**, **2** and **4**.

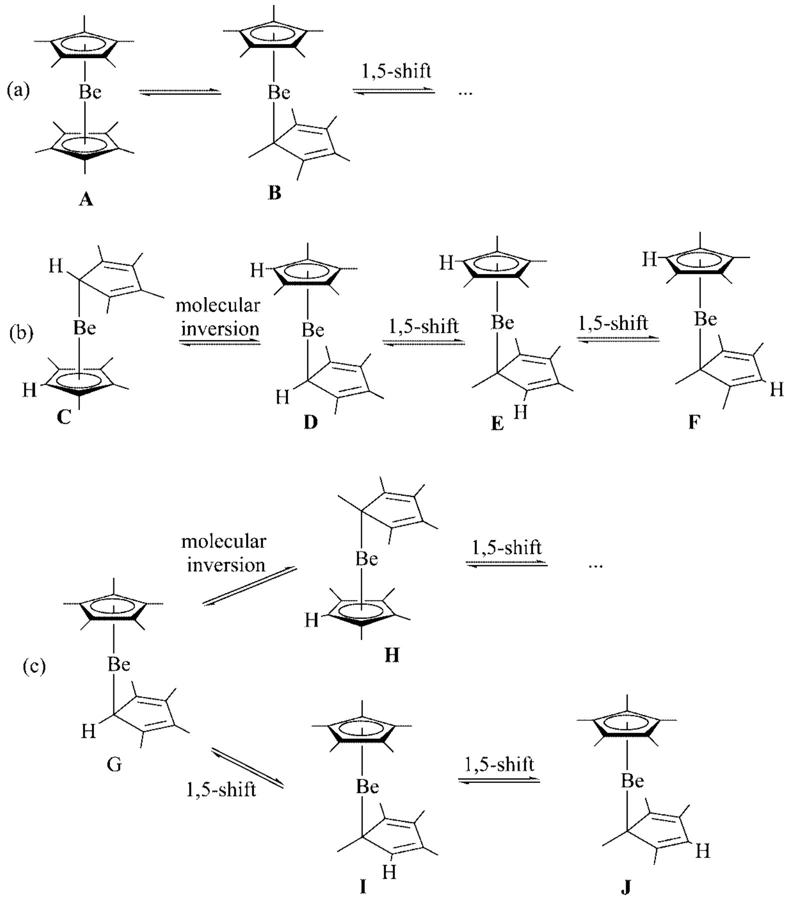
In contrast with beryllocenes **1**, **2** and **4**, [Be(C_5Me_5)$_2$] (**3**) exhibits an almost regular, ferrocene-like, sandwich structure in the solid state (Figure 1). The two C_5Me_5 rings are perfectly parallel and planar (the average deviation from the mean plane is 0.01 Å) and are separated by 3.310(1) Å, a distance comparable to the 3.35 Å interlayer gap in graphite.[34] The Be–C_5Me_5 centroid distance of 1.655(1) Å is noticeably longer than the Be–Cp′ centroid separations in **2** and **4** (ca. 1.47 Å), thus revealing a significantly weaker Be–C_5Me_5 bonding interaction. This is not unexpected, however, in view of the existence of two π-C_5Me_5 rings in the molecules of **3** (formal coordination number of six) and of only four valence orbitals on beryllium. The relatively long Be–C_5Me_5 centroid and Be–C distances in **3** are not abnormal. As a matter of fact, they are comparable to those found in the known compounds [Mg(C_5Me_5)$_2$][35] and [Al(C_5Me_5)$_2$]$^+$[36] if the differences in the ionic radii of the three metal ions are taken into account. Be^{2+}, when six coordinate, has an (estimated) effective ionic radius[27] of 0.45 Å, Al^{3+} of 0.535 Å and Mg^{2+} of 0.72 Å. Using an estimated value of 1.63 Å for the "ionic radius" of the ring carbon atoms[37] of the $C_5Me_5^-$ group in these compounds,[29] M–C(η^5) distances of 2.08 Å (Be), 2.16 Å (Al) and 2.35 Å (Mg) can be calculated that are in excellent agreement with the experimental values (2.05 Å in the Be, 2.16 Å in the Al and 2.34 Å in the Mg metallocenes).

Solid-state ^{9}Be and ^{13}C NMR studies have also been employed to elucidate the structure and dynamics of the methyl-substituted beryllocenes **2** and **3**, as well as the parent beryllocene.[15] Interestingly, within the relatively small chemical-shift range of ^{9}Be (ca. +25 to –25 ppm) the isotropic chemical shift has been found to vary with the coordination of the Cp′ rings from, for instance, $\delta = -19.8$ ppm in the η^5/η^1 beryllocene **2** to $\delta = -24.4$ ppm in the η^5/η^5 compound **3**. It was also found that the Cp′ rings of **2** feature relatively little motion in the temperature interval from –100 to 80 °C, while in the case of **3** the rate of reorientation of the C_5Me_5 rings decreases substantially at low temperatures.[15]

The bonding in decamethylberyllocene (**3**) has been analysed at different levels of theory and the geometry of its molecules optimised enforcing the η^5/η^5 D_{5d} and the η^5/η^1 C_s symmetries. The B3LYP functional predicts the C_s structure to be the lower energy one by about 3 kcal mol^{-1}, whereas calculations with the PW91 functional lead to a difference of only 1 kcal mol^{-1}. This is consistent with the very fluxional structures of beryllocenes. The very low energy difference between the two geometries suggests that the compression implied by crystal packing may distort the molecules toward the observed η^5/η^5 geometry. The calculations also showed that the electrostatic contribution to the bonding ($Be^{2+}\cdots 2\ C_5Me_5^-$) for the D_{5d} structures of $[Be(C_5H_5)_2]$ and $[Be(C_5Me_5)_2]$ amounts to around 65 and 58 %, respectively. Thus, it is clear that the bonding in **1** and **3** has a high covalent character and that the covalency is larger in $[Be(C_5Me_5)_2]$ than in $[Be(C_5H_5)_2]$.[29]

Variable temperature ^{1}H and ^{13}C NMR spectroscopy and reactivity studies are in agreement with the expected fluxionality for these molecules, consisting of two very low-energy processes: a 1,5-sigmatropic shift of the Be(η^5-Cp′) fragment around the periphery of the η^1 ring and the "molecular inversion" that results in the exchange of the two rings.[21] For the parent beryllocene the rates of molecular redistribution in solution[20] (300 K) and in the gas phase (400 K) are of the order of 10^{10}–10^{12} s^{-1} and therefore the processes cannot be detected by NMR methods.

In accordance with this, the two rings of $[Be(C_5Me_4H)_2]$ are equivalent (from –90 to +80 °C) and experience very little chemical-shift variation. Decamethylberyllocene shows a singlet in the ^{1}H NMR spectrum ($\delta = 1.9$–2.0 ppm between –90 and +80 °C) and a unique ^{13}C resonance for the ring carbon nuclei ($\delta = 109.7$ ppm at –90 °C). Naturally, this cannot be taken as being suggestive of fluxionality, but by similarity with the other beryllocenes it is reasonable to assume that the η^5/η^5 and η^5/η^1 structures exist in equilibrium in solution. For the mixed-ring beryllocene **4**, an important contribution of the η^5-C_5Me_5/η^1-C_5Me_4H solid-state structure to the solution structure has been proposed from the variable temperature ^{1}H and $^{13}C\{^1H\}$ chemical shifts and also from the observation of a well-resolved coupling (10 Hz) between the quadrupolar ^{9}Be and the ^{13}CH nuclei in the $^{13}C\{^1H\}$ NMR spectrum recorded at +95 °C.



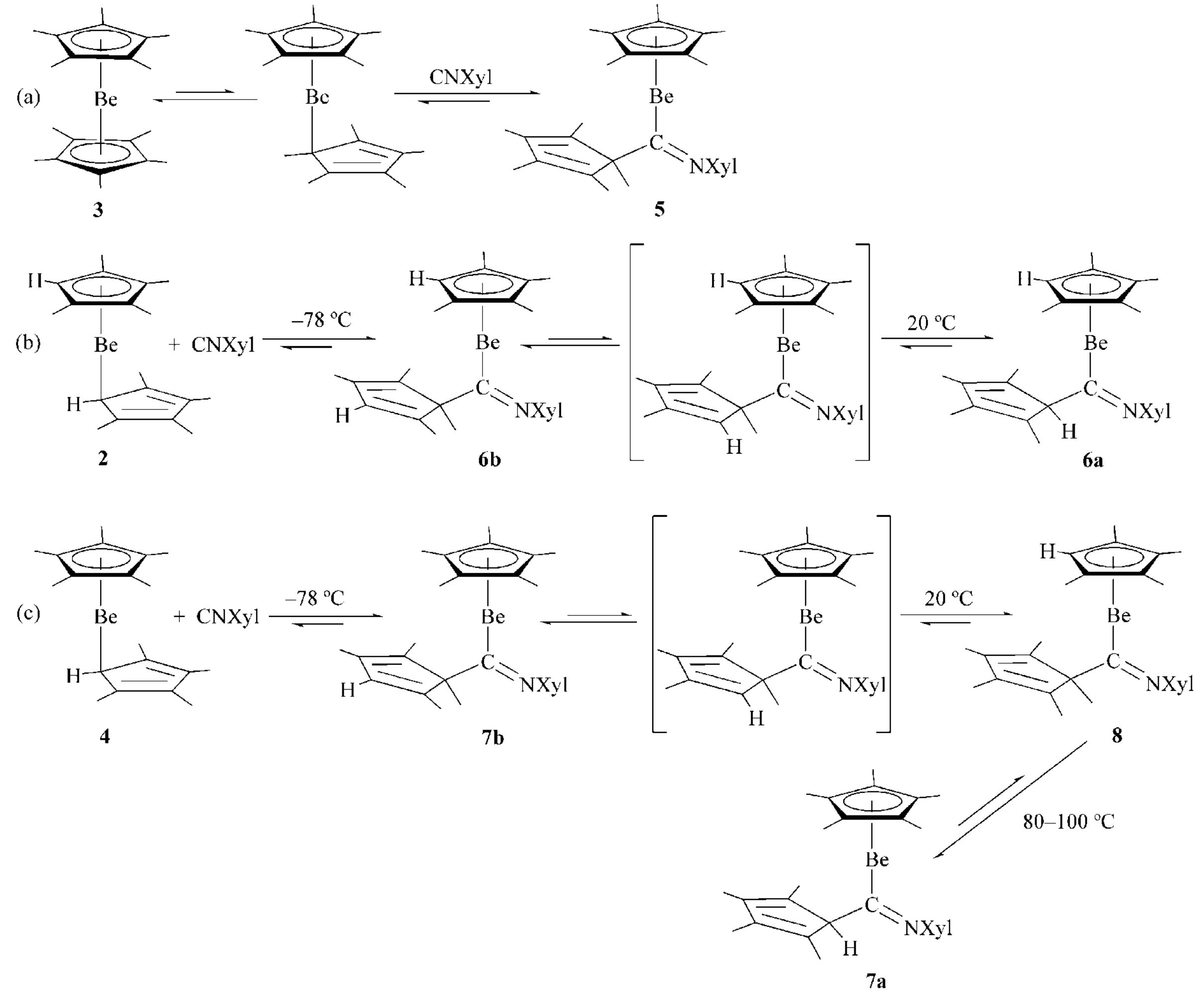
Scheme 2. Rearrangements of substituted beryllocenes: a) $[Be(C_5Me_5)_2]$; b) $[Be(C_5Me_4H)_2]$; c) $[Be(C_5Me_5)(C_5Me_4H)]$.

Reactions of $[Be(C_5Me_4H)_2]$, $[Be(C_5Me_5)_2]$ and $[Be(C_5Me_5)(C_5Me_4H)]$ with CNXyl: The Half-Sandwich Beryllocenes $[Be(\eta^5\text{-}Cp')\{C(NXyl)Cp''\}]$

The above-mentioned dynamic processes that account for the fluxionality of the beryllocenes should give rise to different isomeric structures (Scheme 2) in the solutions of **2**, **3** and **4**. Interestingly, the study of the reactions of these compounds with CNXyl (Xyl = C_6H_3-2,6-Me_2) could be taken to support the existence of most of these structures in solution and has therefore been employed as a chemical probe for both the sigmatropic shift and the molecular-inversion rearrangements that form them.[38] This relies on the assumption that formation of the iminoacyl complexes (see below) occurs by direct attack of CNXyl on a Be–η^1-Cp′ bond, without a change in the coordination of the η^5-Cp′ ring.

The permethylated beryllocene **3** and CNXyl react at room temperature to form the iminoacyl complex **5** (Scheme 3a). The reaction is reversible and the equilibriumis characterised by $\Delta H°$ and $\Delta S°$ values of 18(0.4) kcal mol^{-1} and 35(1) cal mol^{-1} K^{-1}, respectively. The reaction of $[Be(C_5Me_4H)_2]$ (**2**) and CNXyl is also reversible (Scheme 3b). However, due to the lower symmetry of the C_5Me_4H group, this system is somewhat more complex and three iminoacyl isomers are possible. Two of them, **6a** and **6b**, have been isolated and characterised. Even though variable temperature ^1H NMR monitoring of the reaction suggested the formation of another product, its characterisation was not possible. Mechanistically, CNXyl attack on a Be–η^1-Cp′ bond was suggested to explain iminoacyl formation rather than a migratory insertion reaction on the basis of steric crowding around the metal and the availability of only four valence orbitals. Regardless of this, since a Be–η^1-Cp′ bond participates in the C–C coupling, the formation of iminoacyls **5** and **6** (Scheme 3a and b) suggests the existence in solution of the η^5/η^1 structures **B** (in the case of **3**) and **D** and **F** (for **2**) resulting from the 1,5-sigmatropic shift (Scheme 2a and b).

Naturally, the identity of the two Cp′ rings of **2** and **3** does not permit detection of the "molecular inversion" rearrangement that interchanges the two rings. Nonamethylberyllocene (**4**) is therefore unique in this regard. As shown in Scheme 3c, four isomeric iminoacyl complexes are possible and, indeed, the treatment of **4** with CNXyl has allowed the isolation of three of them. As could be antici-



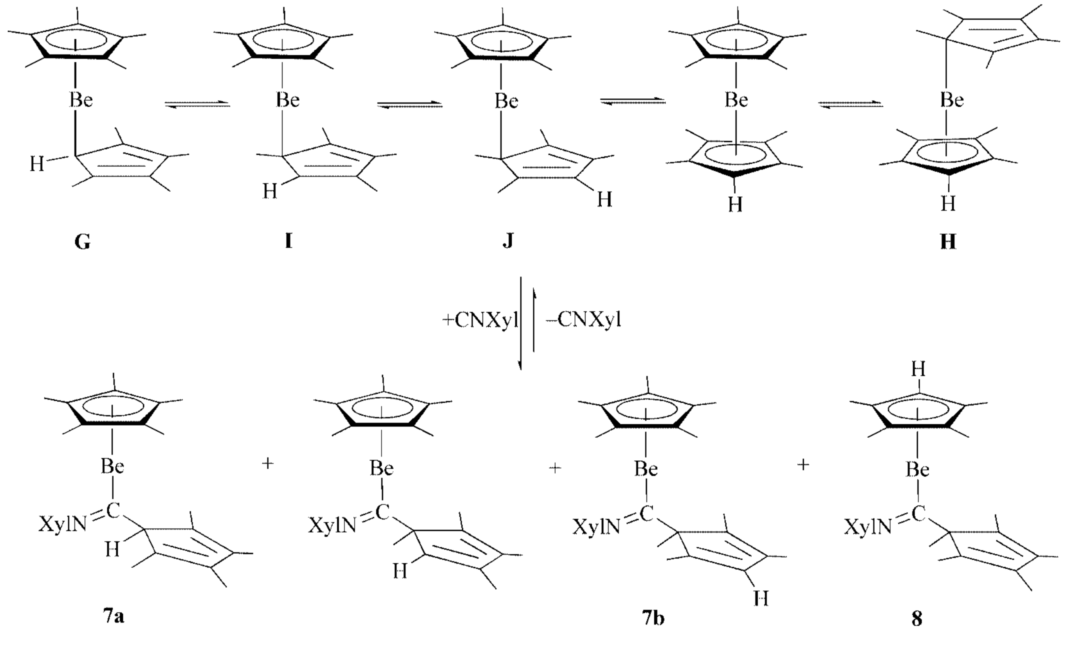
Scheme 3. Reaction of $[Be(C_5Me_5)_2]$ (**3**), $[Be(C_5Me_4H)_2]$ (**2**) and $[Be(C_5Me_5)(C_5Me_4H)]$ (**4**) with CNXyl.

pated, the thermodynamic isomer **7a** contains an η^5-C_5Me_5 ligand and an iminoacyl fragment that results from C–C coupling between the CH unit of C_5Me_4H and CNXyl. Most interestingly, however, compound **8**, which is generated in the room temperature reaction, has an η^5-C_5Me_4H ring and a C(NXyl)C_5Me_5 iminoacyl ligand, thus indicating that the "inverted" beryllocene structure **H** of Scheme 2c is attainable in solution.

Summarizing the reactivity of beryllocenes represented in Schemes 2 and 3, the formation of iminoacyls **5**–**8** can be accounted for by assuming that iminoacyl formation is a reversible process, as has been convincingly demonstrated. The generation of the different isomers may be explained in relatively simple terms with the aid of Scheme 4 for the particular example of the reaction of **4** with CNXyl. It can be proposed that the different η^5/η^1 beryllocene isomers that may exist in solution (**G**, **H**, **I** and **J**) compete for the isocyanide, so that at a certain temperature the outcome of the reaction depends upon: i) the accessibility of the particular isomer, i.e. its population, and the activation barrier of its C–C coupling reaction, and ii) the thermodynamic stability of the resulting iminoacyl relative to that of the other isomers. For instance, the seemingly exclusive formation of **7b** at –78 °C suggests that its η^5/η^1 beryllocene precursor **J** is accessible at this temperature and, moreover, that it features the lowest barrier of all C–C couplings. Since the formation of **7b** is reversible, other less-facile C–C couplings may occur at higher temperature, for instance that leading to the "inverted" compound **8**. Finally, since the formation of **7a** requires heating at 80–100 °C, it appears that the strongest Be–CH bond of those possible for the Be–η^1-C_5Me_4H unit is the most reluctant to participate in the C–C coupling with CNXyl.

Other Half-Sandwich Cyclopentadienylberyllium Compounds

A large number of beryllium compounds containing only one cyclopentadienyl ligand have been described, mainly by the groups of Morgan, Coates and Gaines, and they have been considered in previous review articles.[4] Therefore, only a brief, non-comprehensive coverage is presented here. Most of these compounds have been prepared by the reaction between beryllocene and the corresponding disubstituted beryllium compound BeR_2, leading to the mixed products [BeCpR] with R = H,[39] Cl,[40] Br,[41] I,[42] CH_3,[11,39b] *t*Bu,[43] C_6F_5,[43] C_6H_5,[44] C≡CH,[45] and C≡C–CH_3.[45] Other half-sandwich beryllium complexes containing different borate ligands have been synthesised by other routes. For example, reaction of [BeCpCl] with $LiBH_4$ and KB_5H_8 leads to the complexes [BeCp(BH_4)][46] and [BeCp(B_5H_8)],[47] respectively. The synthesis of compounds [BeCp(B_3H_8)][48] and [BeCp(B_5H_{10})][49] has been achieved by the reaction of NaCp with [Be(B_3H_8)$_2$] and [BeBr(B_5H_{10})], respectively. The amide complexes [BeCp(NMe_2)], [BeCp(NEt_2)], [BeCp(NPh_2)] and [BeCp{N($SiMe_3$)$_2$}] have been prepared by mixing equimolar amounts of the corresponding Li or Na amide and [BeCpX] (X = Cl, Br). They can also be prepared by stirring an equimolar mixture of beryllocene and the corresponding beryllium bis(amide) complex.[50] Recently, the complex [BeCp($SiMe_3$)] has been synthesised[51] by the base-free reaction of [$LiSiMe_3$] with [BeCpCl]. It constitutes the first example of a compound with a direct Be–Si bond[51] and it is characterised by an Si–Be distance of 2.18 Å, which is significantly longer than the sum of the covalent radii (2.01 Å).



Scheme 4. Reaction of the possible isomers of **4** with CNXyl.

All these cyclopentadienyl half-sandwich complexes are air-sensitive, colourless solids or liquids whose structural parameters are available mainly from X-ray structural data[47,51,52] and from electron diffraction and microwave studies.[39a,40–42,53] In nearly all cases the molecules are monomeric in the solid state, in solution, and in the gas phase, with pentahapto coordination of the cyclopentadienyl ligand. The beryllium to ring centroid distances (e.g. $[BeCpCl]_{(g)}$ 1.48 Å;[39a] $[BeCpCl]_{(s)}$ 1.45 Å;[52] $[BeCpBr]_{(g)}$ 1.53 Å;[40] $[BeCpMe]_{(g)}$ 1.50 Å;[11] $[BeCpCCH]_{(g)}$ 1.49 Å;[40] $[BeCpB_5H_8]_{(s)}$ 1.47 Å[46]) are all similar to that to the nearest ring in beryllocene[14] (1.505 Å). The Be–CH_3 bond length in [BeCpMe] is not significantly different from the Be–C bond length in dimethylberyllium [1.698(5) Å], but the Be–Cl bond length in [BeCpCl] is significantly longer in the gas phase [1.837(6) Å] and in the solid state [1.869(3) Å] than in monomeric beryllium dichloride (1.75 Å). It seems reasonable to assume that the dative Cl–Be π-bonding interaction is weaker in [BeCpCl] than in $BeCl_2$.

The most notable feature of the NMR spectrum of these compounds is that in the ^{13}C NMR spectrum of [BeCpBr], a ^{13}C–^{9}Be coupling of 1.1 Hz has been observed.[54] $[BeCpBH_4]$ is unique in exhibiting a very well-resolved ^{9}Be NMR multiplet spectrum and is the only known example of ^{9}Be–^{11}B coupling (3.6 Hz), as a 1:1:1:1 quartet and an unresolved ^{9}Be–^{10}B septet of equal intensity of 1.2 Hz are also observed.[57b] The ^{9}Be and ^{29}Si NMR spectra[51] of $[BeCp(SiMe_3)]$ exhibit a large J(Be–Si) coupling constant of 51 Hz, and the ^{9}Be chemical shift of δ = –27.70 ppm is the highest-field value recorded to date, in accordance with the calculated bond-polarity pattern as well as a bond to Si.

Theoretical calculations at different levels have been performed for monocyclopentadienylberyllium compounds, especially for [BeCpH].[9c] It has been shown that [BeCpH] strongly prefers C_{5v} symmetry and pentahapto bonding with a high degree of covalent character. Bonding between beryllium and the monodentate ligand involves one sp hybrid orbital on the metal while the other sp hybrid interacts with the $a_1\pi$ orbital of the ring. The remaining 2p orbitals on beryllium overlap with filled $e_1\pi$ orbitals to form degenerate bonding orbitals. Beryllium is therefore surrounded by an octet of electrons and since these compounds are not electron deficient, there is relatively little tendency for association or complex formation.[11,39a,40,55]

In contrast to the many known organoberyllium compounds that contain a Be(η^5-C_5H_5) fragment,[4] there are only a few in which the cyclopentadienyl ligand is substituted. The half-sandwich species [Be(η^5-C_5Me_5)Cl] (**9a**) was first isolated by Burns and Andersen in 1987,[28] and later used by Pratten, Cooper and Aroney, to prepare the mixed-ring beryllocene [Be(C_5Me_5)(C_5H_5)], which they characterised by solution IR and NMR studies.[26] The organometallic beryllium compounds [Be(η^5-C_5Me_5)Me],[28] [Be(η^5-C_5Me_5)(P*t*Bu_2)][56a] and [Be(η^5-C_5Me_5)(As*t*Bu_2)][56b] were subsequently prepared from **9a**.

The complexes [Be(η^5-C_5Me_5)X] [X = Cl (**9a**), Br (**9b**)] are obtained in high yields when $[BeX_2(OEt_2)_2]$ (X = Cl, Br) are allowed to react with [M(C_5Me_5)] salts (M = Na, K). The alkyl derivatives [Be(η^5-C_5Me_5)R] [R = Me (**10a**), CMe_3 (**10b**), CH_2CMe_3 (**10c**), CH_2Ph (**10d**)] can then be obtained by metathetical exchange with an alkyllithium reagent in Et_2O.[38] Compounds **9** and **10** are crystalline solids, which may be crystallised by cooling their concentrated pentane solutions.

The NMR spectroscopic data for compounds **9** and **10** (^{1}H, ^{13}C and ^{9}Be)[38] compare well with those reported for other Cp′–Be derivatives. The ^{13}C chemical shift of the Me group of [Be(η^5-C_5Me_5)Me] (**5a**) is δ = –25.4 ppm and the signal appears as a well-resolved 1:1:1:1 pattern due to coupling to ^{9}Be (I = 3/2), with a ^{1}J(Be–C) coupling constant of 30 Hz. In all of the other alkyls this resonance was not observed, presumably due to quadrupolar relaxation by the beryllium nucleus. The ring carbon atoms are not affected by the quadrupolar nucleus since the singlet resonances are sharp and no coupling is detected. The chemical shift value of δ = 108–109 ppm is almost the same as that found for structurally characterised Be(η^5-C_5Me_5) compounds.[28] The ^{9}Be chemical shifts also have normal values. The signals are relatively sharp (half-height width of 3.5 Hz for **9b** and 16 Hz for **10a**) and, due to paramagnetic ring-current effects,[41,57] they are located in the higher-field region of the ^{9}Be chemical shift range (from approximately δ = –25 to +25 ppm).[20,41,57–59]

Both the halides **9** and the alkyls **10** are stable toward disproportionation. In an attempt to obtain the hydride [Be(η^5-C_5Me_5)H], which is isolobal with the alkyls **10**, Andersen et al. treated [Be(η^5-C_5Me_5)Br] with LiAlH. IR studies on the crude reaction product revealed the existence of absorptions at 1950–1985 cm^{-1} that could be due to a Be–H group.[38] However, no hydride resonance could be found by ^{1}H NMR spectroscopy. Instead, the ^{1}H, ^{9}Be and $^{13}C\{^{1}H\}$ NMR spectra of the mixture confirmed the existence of $[Be(C_5Me_5)_2]$ and [Be(C_5Me_5)Br]. Thus, it is possible that [Be(η^5-C_5Me_5)H] forms but it is not stable at room temperature and disproportionates to $[Be(C_5Me_5)_2]$ and BeH_2.

Summary and Outlook

Since 1959, and for a period of over forty years, beryllocene $[Be(C_5H_5)_2]$ (**1**) has been the only member of the beryllocene family of compounds. This singularity, and above all its unusual structure, has motivated an astonishingly large number of both experimental and theoretical investigations.

The preliminary studies reported by our group in 2000 constituted a major turn-about of this situation since synthetic and structural data for two new beryllocenes were provided.[29b] Like **1**, the new beryllocenes, viz. $[Be(C_5Me_4H)_2]$ (**2**) and $[Be(C_5Me_5)_2]$ (**3**), contain two Cp′ rings of the same kind. Shortly afterwards, preliminary information on the structure and chemical behaviour of the mixed-ring compound [Be(η^5-C_5Me_5)(η^1-C_5Me_4H)] (**4**) was also provided by our group.[38b]

The beryllocenes that possess one or two C_5Me_4H rings, i.e. **2** and **4**, feature η^5/η^1 geometries of the slipped-sandwich type, with the η^1-C_5Me_4H ligand bonded to beryllium through the unique CH carbon atom.[29,38] At variance with the parent beryllocene **1**, the structures of **2** and **4** exhibit no positional or thermal disorder. The calculated geometries are in agreement with experimentally observed structures and the calculations reveal that the preference of beryllium for CH binding is due to larger charge localisation on this part of the η^1 ring.

In contrast with this situation, the long sought-after decamethylberyllocene $[Be(C_5Me_5)_2]$ (**3**) has an almost regular sandwich structure in the solid state.[29] Possibly, crystal packing effects may originate steric repulsions between the methyl ring substituents that force the molecules of **3** to adopt the η^5/η^5 geometry in the condensed state. This distortion would be energetically facile as the calculated energy difference between the two geometries is very low.

The half-sandwich chloride derivative $[Be(\eta^5\text{-}C_5Me_5)Cl]$ reported by Burns and Andersen[28] in 1987, and the bromide analogue,[38a] are key reagents for $Be(\eta^5\text{-}C_5Me_5)$ chemistry. These compounds have been used as precursors for the synthesis of a number of $Be(\eta^5\text{-}C_5Me_5)$ organometallics, including the alkyls $[Be(\eta^5\text{-}C_5Me_5)R]$ and the beryllocenes $[Be(C_5Me_5)_2]$, $[Be(C_5Me_5)(C_5Me_4H)]$ and $[Be(C_5Me_5)(C_5H_5)]$. It is foreseeable that they will continue to play a major role in future $Be(\eta^5\text{-}C_5Me_5)$ chemistry.

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