Synthesis, Solid-State Structure, and Bonding Analysis of the Beryllocenes $[Be(C_5Me_4H)_2]$, $[Be(C_5Me_5)_2]$, and $[Be(C_5Me_5)(C_5Me_4H)]$

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In memory of Professor Sir Geoffrey Wilkinson

Abstract: The beryllocenes $[Be(C_5Me_4H)_2]$ (**1**), $[Be(C_5Me_5)_2]$ (**2**), and $[Be(C_5Me_5)(C_5Me_4H)]$ (**3**) have been prepared from $BeCl_2$ and the appropriate KCp′ reagent in toluene/diethyl ether solvent mixtures. The synthesis of **1** is facile (20 °C, overnight), but generation of decamethylberyllocene **2** demands high temperatures (ca. 115 °C) and extended reaction times (3–4 days). The mixed-ring beryllocene **3** is obtained when the known $[(\eta^5\text{-}C_5Me_5)BeCl]$ is allowed to react with $K[C_5Me_4H]$, once more under somewhat forcing conditions (115 °C, 36 h). The structures of the three metallocenes have been determined by low-temperature X-ray studies. Both **1** and **3** present η^5/η^1 geometries of the slip-sandwich type, whereas **2** exhibits an almost regular, ferrocene-like, sandwich structure. In the mixed-ring compound **3**, C_5Me_5 is centrally bound to beryllium and the $\eta^1\text{-}C_5Me_4H$ ring bonds to the metal through the unique CH carbon atom. This is also the binding mode of the η^1-ring of **1**. To analyze the nature of the bonding in these molecules, theoretical calculations at different levels of theory have been performed on compounds **2** and **3**, and a comparison with the bonding in $[Be(C_5H_5)_2]$ has been made. As for the latter molecule, energy differences between the η^5/η^5 and the η^5/η^1 structures of **2** are very small, being of the order of a few kcal mol^{-1}. Constrained space orbital variations (CSOV) calculations show that the covalent character in the bonding is larger for $[Be(C_5Me_5)_2]$ than for $[Be(C_5H_5)_2]$ due to larger charge delocalization and to increased polarizability of the C_5Me_5 fragment.

Keywords: beryllium · cyclopentadienyl ligands · electronic structure · metallocenes · X-ray diffraction

Introduction

The cyclopentadienyl derivatives of the alkaline-earth metals, MCp'_2, are an attractive family of metallocenes that has experienced a remarkable development over the last two decades.[1] The use of substituted cyclopentadienyl ligands, including those with very bulky substituents,[2] has added luster to this field and has permitted the stabilization of fascinating hitherto unknown structures[1, 3] that actually emerge from a seemingly simple electrostatic, $M^{2+}\cdots 2\,Cp'^-$ bonding model.[1a] Indeed, theory suggests[4] that with the exception of the more covalent $[Be(C_5H_5)_2]$, electrostatic forces in the unsubstituted metallocenes, $[M(C_5H_5)_2]$, of Mg to Ba account for approximately 70–85 % of the total interaction energy.[4a]

By using Cp′ ligands with different substituents and variable degrees of substitution, many MCp'_2 compounds of the alkaline-earth elements from Mg to Ba have been structurally characterized in the solid state by X-ray methods. It is therefore surprising that prior to this work $[Be(C_5H_5)_2]$ was the only beryllocene authenticated by X-ray crystallography.[5, 6] It appears plausible that the widely accepted belief that the tiny Be^{2+} ion, which is the smallest of the dipositive cations,[7b] could not accommodate two bulky Cp′ rings may have deterred studies aimed at the preparation of beryllocenes with substituted cyclopentadienyl ligands.[8] In accord

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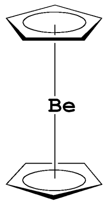
with these premises only the half-sandwich complex [Be(η^5-C_5Me_5)Cl], could be isolated from the treatment of $BeCl_2$ with C_5Me_5 transfer reagents, under different reaction conditions.[9, 10] However, the mixed-ring complex [Be(C_5Me_5)(C_5H_5)] was obtained when [Be(η^5-C_5H_5)Cl] and Li[C_5Me_5] were allowed to react in the absence of solvent (60 °C, melted mixture).[10]

The structure of beryllocene has been the subject of an intense debate since its first preparation by Fischer and Hoffmann in 1959.[11] The different nature of the two C_5H_5 rings is manifested by the observation of a high dipole moment in solution[11] (2.24 D, cyclohexane, 25 °C), which rules out the symmetrical ferrocene-like structure **I**. Three X-ray studies[5] have demonstrated the adoption of the slip-sandwich $\eta^5/\eta^1(\pi)$ structure **II** with the beryllium atom disordered between two equivalent sites of 50% occupancy. Reinterpretation of the electron diffraction data leads also to a slipped-sandwich geometry for the molecules of [Be(C_5H_5)$_2$] in the gas phase.[12] This unusual structure has been lucidly rationalized by Beattie and Nugent,[13] and finds additional theoretical support in recent molecular dynamic[14] and DFT calculations.[4a]



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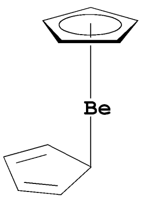

II

Abstract in Spanish: *Los berilocenos [Be(C_5Me_4H)$_2$] (**1**), [Be(C_5Me_5)$_2$] (**2**) y [Be(C_5Me_5)(C_5Me_4H)] (**3**) se preparan mediante la reacción del $BeCl_2$ con el reactivo KCp' apropiado, usando mezclas de tolueno y éter como disolvente. Aunque la síntesis del compuesto **1** ocurre bajo condiciones de reacción suaves (20 °C, 12 h), la del decametilberiloceno **2** requiere altas temperaturas (~115 °C) y tiempos de reacción prolongados (3–4 días). El beriloceno mixto **3** se obtiene a partir del compuesto [(η^5-C_5Me_5)BeCl], por reacción con K[C_5Me_4H], a 115 °C durante aproximadamente 36 h. La estructura de las moléculas de estos berilocenos en el estado sólido se ha determinado mediante estudios de difracción de rayos X, efectuados a temperaturas bajas. Tanto el compuesto **1** como el **3** poseen geometría η^5/η^1 de tipo "slip-sandwich", mientras que la del **2** es casi regular, de tipo η^5/η^5. En el compuesto **3** el anillo de C_5Me_5 se coordina de manera simétrica (η^5) pero el de C_5Me_4H se une al berilio a través del átomo de C de la agrupación CH. Con la finalidad de analizar la naturaleza del enlace Be–Cp' se han desarrollado cálculos teóricos de diferente complejidad para los compuestos **2** y **3**, y se han comparado los resultados obtenidos con los correspondientes al [Be(C_5H_5)$_2$]. Al igual que en esta última molécula, las diferencias de energía entre las estructuras η^5/η^5 y η^5/η^1 del compuesto **2** son muy pequeñas, del orden de algunas kcal mol^{-1}. Los cálculos de tipo "Constrained Space Orbital Variations" (CSOV) ponen de manifiesto que el carácter covalente del enlace en el [Be(C_5Me_5)$_2$] es mayor que en el [Be(C_5H_5)$_2$], debido probablemente a una deslocalización superior de la carga en el primero y a la mayor polarizabilidad del grupo C_5Me_5 en comparación con el C_5H_5.*

In solution, beryllocene is a highly fluxional molecule. Only one set of resonances is found for the two C_5H_5 groups in the ^1H and ^{13}C NMR spectra down to −135 °C,[15] as a consequence of two facile rearrangements. These are a 1,5-sigmatropic shift of the Be(η^5-C_5H_5) unit around the periphery of the η^1-C_5H_5 ring and a molecular inversion that interchanges the η^5 and the η^1 rings.[14] The rates for molecular redistribution in solution (300 K)[15b] and in the gas phase (400 K)[14] are of the order of 10^{10}–10^{12} s^{-1}, making detection by NMR impossible.

The successful use of methyl-substituted cyclopentadienyl ligands, in particular of C_5Me_5, for the development of main group metallocenes,[1, 8, 16] led us to attempt the preparation of the beryllocenes of C_5Me_4H and C_5Me_5. Herein we present the synthesis and structural characterization of three new beryllocenes, namely [Be(C_5Me_4H)$_2$] (**1**), [Be(C_5Me_5)$_2$] (**2**), and [Be(C_5Me_5)(C_5Me_4H)] (**3**). Detailed theoretical calculations aimed to shed some light on the electronic factors governing the preference for η^5-η^5 or η^5-η^1 structures and to analyze the nature of the bonding in these systems will also be presented. Part of this work has appeared in preliminary form.[17]

Results and Discussion

Synthesis and properties of [Be(C_5Me_4H)$_2$] (1), [Be(C_5Me_5)$_2$] (2), and [Be(C_5Me_5)(C_5Me_4H)] (3): Despite the long controversy surrounding the structure of [Be(C_5H_5)$_2$] and the existence of many half-sandwich beryllium compounds,[6] at the outset of this work no other beryllocenes had been reported, with the exception of [Be(C_5Me_5)(C_5H_5)], characterized only in solution.[10] Related dihydro-1*H*-azaboryl species had also been investigated.[18]

Octamethylberyllocene, [Be(C_5Me_4H)$_2$] (**1**), can be synthesized by the reaction of $BeCl_2$ and K[C_5Me_4H] in diethyl ether as the solvent. As shown in Equation (1), overnight room temperature conditions suffice to prepare this compound in good yields (isolated yield of 70%).

$$BeCl_2 + 2K[C_5Me_4H] \xrightarrow[12\ h]{20\ ^\circ C} \underset{\mathbf{1}}{[Be(C_5Me_4H)_2]} + 2KCl \qquad (1)$$

Complex **1** is a low-melting (83 °C), volatile, sublimable material that is very soluble in common non-polar organic solvents. It is very reactive towards O_2 and H_2O and decomposes immediately upon exposure to air. In toluene solution it is highly fluxional, only one set of signals can be detected for the two C_5Me_4H groups in the ^1H and ^{13}C NMR spectra down to −90 °C. There is little variation of the chemical shift with temperature. For instance, the two different *C*Me nuclei within each ring resonate at $\delta = 117.2$ and 117.3 ppm at 80 °C and $\delta = 117.8$ and 118.7 ppm at -90 °C. A somewhat larger variation is found for the *C*H resonance, which changes from $\delta = 84.7$ ppm (80 °C) to $\delta = 80.4$ ppm (-90 °C). In the same temperature range the one-bond ^{1}J(C,H) coupling constant experiences no appreciable change (ca. 157 Hz). For comparative purposes the corresponding resonances of [Mg(η^5-$C_5Me_4H)_2$][19a] are approximately $\delta =$ 102 (*C*H, 163 Hz) and 112.3, 112.5 ppm (*C*Me). In isomeric iminoacyl derivatives of composition [Be(η^5-C_5Me_4H)(C(N-Xyl)C_5Me_4H)][20] (Xyl = Me_2-2,6-C_6H_3), the η^5-C_5Me_4H ligand displays ^{13}C signals at approximately $\delta = 101$ (*C*H) and 109–111 ppm (CMe). Since a Be-η^1-C_5Me_4H linkage is expected to give higher-field *C*H and lower field *C*Me resonances, the observed NMR data for **1** seem to correspond to the expected average of the η^5- and η^1-bonded C_5Me_4H rings. The solution dynamic behavior of **1** is likely to involve a 1,5-sigmatropic shift of the Be(η^5-C_5Me_4H) group around the η^1-C_5Me_4H ligand, plus the exchange of the η^5- and η^1-C_5Me_4H ligands, as proposed for [Be($C_5H_5)_2$].[14] This topic will be discussed in the following paper of this issue.[20] The ready formation of **1** under the mild, room temperature conditions of Equation (1), encouraged us to pursue the synthesis of decamethylberyllocene. The larger solid angle[21] of C_5Me_5 (187 °C), when compared to C_5Me_4H (177 °C), along with the reported formation of [Be(η^5-C_5Me_5)Cl] when $BeCl_2$ and [Mg($C_5Me_5)_2$] are heated under reflux in toluene/Et_2O mixtures,[9] suggested that more severe reaction conditions should be applied. We have found that K[C_5Me_5], the most nucleophilic of the $C_5Me_5^-$ transfer reagents,[16] interacts with $BeCl_2$ at 115 °C (bath temperature) in a toluene-diethyl ether solution for 3–4 days to give moderate isolated yields (ca. 50 %) of [Be($C_5Me_5)_2$] (**2**) (see Eq. (2)].

$$\mathrm{BeCl_2 + 2K[C_5Me_5]} \xrightarrow[\text{3-4 days}]{115\ ^\circ\mathrm{C}} \underset{\textbf{2}}{\mathrm{[Be(C_5Me_5)_2]}} + \mathrm{2KCl} \tag{2}$$

Similar to [Be($C_5Me_4H)_2$], **2** is soluble in nonpolar organic solvents and decomposes instantly upon exposure to the atmosphere. The formation of **2** at 115 °C is still slow and the crude reaction product is sometimes contaminated by small amounts of [Be(C_5Me_5)Cl]. Separation of the two complexes by fractional crystallization is not straightforward but the chloro derivative is more volatile and can be removed by sublimation, facilitating the purification of **2**.

The ^{1}H and ^{13}C NMR spectra of **2** are very simple and show surprisingly little variation with temperature. Thus, the ^{1}H resonance of the methyl proton changes from $\delta = 2.04$ ppm at 80 °C to 1.91 at -90 °C, whereas in the same temperature interval the ^{13}C signal of the ring carbon nuclei varies by only 1 ppm (from $\delta = 110.7$–109.7 ppm). As in [Be(η^5-C_5Me_5)Cl],[9, 10] [Be(η^5-C_5Me_5)(η^1-C_5H_5)][10] and [Be(η^5-C_5Me_5)(C(Nxyl)C_5Me_5)][20] because the η^5-C_5Me_5 ring-carbon signal appears at $\delta = 108$–110 ppm, decamethylberyllocene might seem to contain η^5-C_5Me_5 rings. This is actually found in the solid state (vide infra). Nonetheless, the expected similarity with other beryllocenes, along with the reactivity of **2** toward CNXyl[20] indicate that in the unlikely event that the η^5/η^5 geometry is maintained in solution, it must exist in fast equilibrium with the isomeric η^5/η^1 structure.

To complete our studies on beryllocenes we have prepared the mixed-ring compound nonamethylberyllocene, [Be(C_5Me_5)(C_5Me_4H)] (**3**), by the high-temperature interaction of [Be(C_5Me_5)Cl] and K[C_5Me_4H] [Eq. (3)].

As for **2**, prolonged heating at elevated temperatures is needed, but the reaction gives good isolated yields (ca. 70 %) of the beryllocene. Compound **3** is also a highly crystalline solid, with solubility and other properties similar to those of **1** and **2**.

$$\mathrm{[Be(C_5Me_5)Cl] + K[C_5Me_4H]} \xrightarrow[\text{84 h}]{115\ ^\circ\mathrm{C}} \underset{\textbf{3}}{\mathrm{[Be(C_5Me_5)(C_5Me_4H)]}} + \mathrm{KCl} \tag{3}$$

Variable-temperature ^{1}H and ^{13}C NMR studies are suggestive of fluxional behavior. As for **2**, the signal due to the carbon nuclei of the C_5Me_5 ring varies very little with temperature. The chemical shift value ($\delta = 108.9$ ppm, 20 °C; $\delta = 108.7$ ppm, -90 °C) may be taken as indicative of η^5-C_5Me_5 coordination. Somewhat more pronounced changes are observed for the C_5Me_4H group, whose *C*H carbon resonance moves from $\delta = 67.0$ to 59.3 ppm, upon lowering the temperature from +95 to -90 °C. No significant variation in the value of ^{1}J(C, H) (ca. 143 Hz) accompanies this chemical shift change. Smaller δ variations are recorded for the *C*Me nuclei (2–4 ppm to lower field from +95 to -90 °C). Comparison of the δ values of the C_5Me_4H ring carbon atoms of **3** at the latter temperature ($\delta = 128.1$, 124.5, and 59.3 ppm) with those of **2** ($\delta = 118.7$, 117.8, and 80.4 ppm) suggests that a [Be(η^5-C_5Me_5)(η^1-C_5Me_4H)] structure, in which Be is bonded to the CH carbon of the η^1-ring, has an important contribution to the solution structure. This assumption finds further support in the observation of a well-resolved coupling of approximately 10 Hz between the quadrupolar ^{9}Be ($I = 3/2$) and the ^{13}C nucleus of the CH group in the ^{13}C NMR spectrum of **3** recorded at +95 °C. For comparative purposes, in the half-sandwich derivative [Be(η^5-C_5Me_5)(CH_3)],[20, 22] ^{1}J(Be, C) for the Be–CH_3 unit amounts to 30 Hz. As already discussed, these data suggest formulation of **3** in solution as [Be(η^5-C_5Me_5)(η^1-C_5Me_4H)] (as shown below, this is the structure of the molecules of **3** in the solid state) and by extension explanation of its dynamic behavior in terms of 1,5-sigmatropic shifts of the Be(η^5-C_5Me_5) group around the periphery of the η^1-C_5Me_4H ring. Nevertheless the results of the DFT calculations that will be discussed later, and the unexpected reactivity of **3** toward CNXyl, that has given rise to three Be-iminoacyl isomers,[20] demostrate that inversion to give [Be(η^5-C_5Me_4H)(η^1-C_5Me_5)] (i.e. ring exchange) is a facile process in solution.

Solid-state structure of beryllocenes 1–3: The structures of metallocenes **1–3** in the solid state have been determined at low-temperature by X-ray crystallography. ORTEP diagrams are given in Figures 1, 2, and 3, crystal data and data collection parameters are presented in Table 1. Table 2 provides a comparison of relevant bonding parameters for the three beryllocenes under discussion.

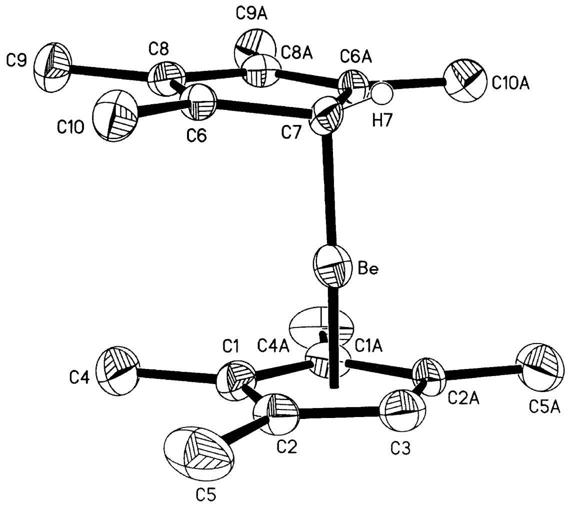

Figure 1. Structure of **1** (ORTEP diagram).

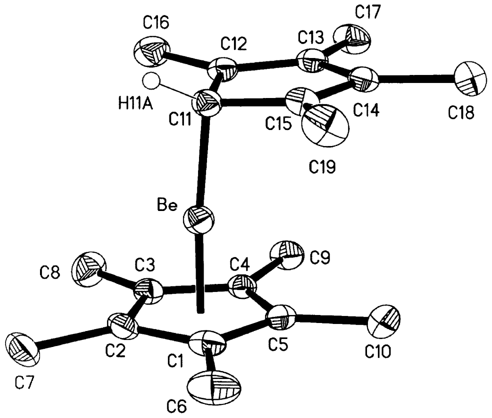

Figure 2. Structure of **3** (ORTEP diagram).

Both $[Be(C_5Me_4H)_2]$ (**1**), and $[Be(C_5Me_5)(C_5Me_4)]$ (**3**) exhibit η^5/η^1 geometries, which in the case of the mixed-ring beryllocene **3** consists of η^5-C_5Me_5 and η^1-C_5Me_4H binding (see Figure 1 and Figure 2). 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 (it is well-known that the strength of the M–C bond decreases with substitution at carbon; primary alkyl compounds are more stable than secondary alkyls and these more than tertiary ones[24]). Interestingly the Be–CH bond lengths are identical within experimental error (Table 2) and compare well with the corresponding length in $[Be(C_5H_5)_2]$ (1.826(6) Å[5]). These Be–CH separations are in the middle of the range of Be–C bond lengths (1.70– 1.85 Å[22, 23]).

The coordination of the η^5-Cp′ ring in **1** and **3** is highly symmetrical. For either compound the five Be–C lengths are almost identical and cluster around 1.90 Å. As can be deduced from the data in Table 2, the difference between the shortest and longest Be–C bonds is only 0.02 Å. Considering that in $[Be(C_5H_5)_2]$, the Be–C(η^5) bond lengths have comparable values (average ca. 1.92 Å) an interesting observation arises, namely that for this series of compounds substitution of H by Me within the η^5-Cp′ ligand does not alter significantly the strength of the Be–C(η^5) bonds. The same conclusion stems from analysis of the separation between Be and the η^5 ring centroids, which is identical in **1** and **3** (1.47 Å) and very similar to that in $[Be(C_5H_5)_2]$ (1.50 Å[5]).

In the two complexes, **1** and **3**, the Be–C(η^1) ring plane angle is close to 100–102°, far from the value of 125° which would be expected for η^1-bonding to a tetrahedral ring carbon atom.[13] Similarly, the Be-C(η^1)-C angles to the adjacent carbon atoms are smaller than the ideal 109.5° value that would correspond to tetrahedral geometry. For instance the Be-C7-C6 angle in **1** is 99.4(3)°, while the analogous Be-C11-C12 angle in **3** amounts 98.4(2)°. Additionally, the η^5 and η^1 rings are almost planar and nearly parallel, the angles between rings being 6.6(1) and 4.9(1)°, for **1** and **3**, respectively. All these data strongly support consideration of the structures of **1** and **3** as of the slipped-sandwich type and therefore similar to that of $[Be(C_5H_5)_2]$.[5] In accord with this, the difference in the length of the $C_{\beta\beta}$ and $C_{\alpha\beta}$ bonds (α and β refer to the position with respect to the Be-bonded carbon atom) is only 0.06–0.07 Å. This contrasts with the significantly larger values found in cyclopentadiene and in cyclopentadienyl rings with localized double bonds. For instance in C_5H_6 this difference is 0.12 Å,[25] whereas in some η^1-Cp′ derivatives such as $[B(\eta^5\text{-}C_5Me_5)(\eta^1\text{-}C_5Me_5)]^+$[26] and $[\{Hg(\eta^1\text{-}C_5Me_4SiMe_2t\text{Bu})Cl\}_4]$[27] it can be as high as approximately 0.14 Å.

Most unexpectedly, and at variance with beryllocenes **1** and **3**, $[Be(C_5Me_5)_2]$ (**2**), exhibits an almost regular, ferrocene-like, sandwich structure in the solid state (Figure 3). 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.[7a] The Be–C_5Me_5 centroid separation of

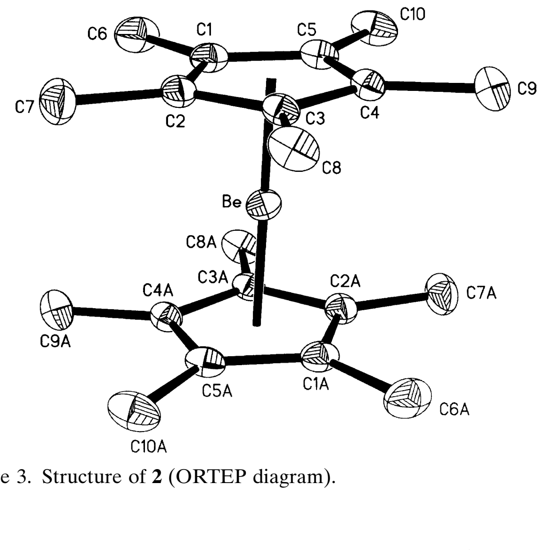

Figure 3. Structure of **2** (ORTEP diagram).

Table 1. Crystal data and structure refinement.

	1	2	3
formula	$C_{18}H_{26}Be$	$C_{20}H_{30}Be$	$C_{19}H_{28}Be$
formula weight	251.40	279.45	265.42
crystal size [mm]	0.10 × 0.20 × 0.20	0.35 × 0.30 × 0.30	0.35 × 0.30 × 0.30
crystal system	orthorhombic	monoclinic	monoclinic
space group	P_{nma}	$C2/c$	$P2_1/n$
a [Å]	12.918(3)	14.9127(5)	8.0745(5)
b [Å]	15.735(3)	11.9919(4)	6.6636(4)
c [Å]	7.621(2)	9.4979(3)	30.295(2)
α [°]	90	90	90
β [°]	90	94.8390(10)	92.097
γ [°]	90	90	90
V [Å^3]	1549.1(5)	1692.47(10)	1628.9(2)
Z	4	4	4
ϱ_{calcd} [Mg m^{-3}]	1078	1097	1082
T [K]	113(2)	103(2)	130(2)
μ [mm^{-1}] (Mo$_{K\alpha}$)	0.059	0.060	0.059
F(000)	552	616	584
$\theta_{\max}$ [°]	20.82	30.68	29.67
index ranges	$-8 \leq h \leq 12$ $-14 \leq k \leq 13$ $-4 \leq l \leq 7$	$-21 \leq h \leq 21$ $-17 \leq k \leq 17$ $-13 \leq l \leq 7$	$-11 \leq h \leq 10$ $-1 \leq k \leq 9$ $-35 \leq l \leq 34$
no. of reflections measured	2661	8398	6690
no. of unique reflections	777	2450	3033
no. of params	98	102	194
R_1 ($I > 2\sigma(I)$)[a]	0.0548	0.0531	0.0672
R_1 (all data)	0.0850	0.0632	0.0844
wR_2 (all data)	0.1637	0.1581	0.1746
diff. Fourier peaks min/max [e Å^{-3}]	−0.216/0.179	−0.355/0.355	−0.239/0.282

[a] $R_1 = \Sigma||F_o| - |F_c||/\sigma|F_o|$, $wR_2 = |\Sigma(w(F_o^2 - F_c^2)^2)/\Sigma(w(F_o^2)^2)]^{1/2}$.

Table 2. Selected bond lengths [Å] and angles [°].

	1	2	3
Be–C(η^5-ring)	1.890(8)–1.911(6)	1.969(1)–2.114(1)	1.896(3)–1.919(3)
Be–Cp′(ring centroid)	1.471(7)	1.655(1)	1.473(4)
Be–C(η^1-ring)	1.769(8)		1.776(3)
centroid-Be-C(η^1) (or centroid-Be -centroid)	176.2(6)	180	175.0(4)
Be-C(η^1)-ring	100.5		102.5

1.655(1) Å is noticeably longer than the Be–Cp′ centroid separations in **1** and **3** (ca. 1.47 Å), thus revealing a significantly weaker Be–C_5Me_5 bonding interaction. This is not unexpected in view of the existence of two π-C_5Me_5 rings in the molecules of **2** (formal coordination number of six) and of only four valence orbitals on beryllium. The Be–C separations are also longer than in **1** and **3** (see Table 2) and the five distances to each ring are not identical but range from 1.969(1) to 2.114(1) Å (average value 2.05 Å; compare to ca. 1.90 Å in **1** and **3**). Consequently the Be–Cp′ centroid vectors are not perpendicular to the ring planes but form an angle of 87.1(5)°. Since theory predicts (vide supra) that the $\eta^5/\eta^1(\pi)$ structure (i.e. the slip-sandwich structure) has minimum energy, crystal packing effects may enforce adoption of the more symmetrical sandwich structure in the solid state. In solution the compound is highly fluxional, as demonstrated by its reactivity toward CNXyl, to be presented in the following paper.[20]

As already stated, the Be–Cp′ centroid and Be–C(η^5) separations in **2** are appreciably longer than in **1** and **3**, and are therefore indicative of a weaker Be–Cp′ bonding interaction. It should be noted, however, that within the variations imposed by the differences in the ionic radii of the metal ions (vide infra), they are comparable to those found in the related [Mg(η^5-C_5Me_5)$_2$][19a] and [Al(η^5-C_5Me_5)$_2$]$^+$[28] species, which are stable molecules that have been known for many years.[19, 28] This similarity becomes even clearer when a comparison of the M–C bond lengths in the three derivatives is made. In the structurally characterized, formally four-coordinate, Be-η^5-C_5Me_5 compounds described in this and in the following paper,[20] as well as in previously reported half-sandwich Be-η^5-C_5Me_5 complexes,[14a, 29] the Be–C separations average approximately 1.90 Å. Since the effective ionic radius of Be^{2+} in four coordination environments is established as 0.27 Å,[7b] following Hanusa[30] a value of 1.63 Å can be estimated for the "ionic radius" of the C atoms of the $C_5Me_5^-$ group. The effective ionic radii, assuming six-coordination for Be^{2+} (0.45 Å, calculated), Al^{3+} (0.535 Å) and Mg^{2+} (0.72 Å),[7b] lead to estimates of M–C(η^5) separations of 2.08 (Be), 2.165 (Al) and 2.35 Å (Mg), which are in excellent agreement with the experimental values (2.05 Å in **2**; 2.16 Å for Al[(η^5-C_5Me_5)$_2$]$^+$[28] and 2.34 Å in [Mg(η^5-C_5Me_5)$_2$][19a]).

Bonding analysis of beryllocenes 2 and 3: comparison with [Be(C_5H_5)$_2$] and [Be(C_5H_5)(C_5MeH_4)]: Although several papers[4, 14] have appeared recently reporting theoretical studies of the geometric and electronic structure of the [Be(C_5H_5)$_2$] complex, to our knowledge, none of them has made an extensive comparison of the electron correlation effects in the theoretical description of this system. For this reason, and to allow a comparison with the results for [Be(C_5Me_5)$_2$], we present in Table 3 the optimized geometries for [Be(C_5H_5)$_2$] and [Be(C_5Me_5)$_2$] at different levels of theory, enforcing either D_{5d} or C_s symmetry.

All the computed geometries for the D_{5d} structures are very similar. The DFT functionals produce the shortest distances, with longer distances computed at the HF level and even longer at the CASSCF level. These results indicate that the effects of the dynamical electron correlation, mostly accounted for in the DFT functionals, increase the strength of the Be–(C_5H_5) and Be–(C_5Me_5) (η^5) delocalized bond, while the non-dynamical correlation effects, included in the CASSCF

Table 3. Calculated main geometrical parameters [Å and °] and relative energies [kcal mol^{-1}] of the C_s isomers.

Molecule/sym	Level	r_{BeC}[a]	r_{BeX}[a]	r_{CC}[a]	α_{XBeC1}[b]	$\beta_{BeC1X'}$[b]	E_{rel}[c]
$[Be(C_5H_5)_2]/D_{5d}$	RHF	2.067	1.685	1.407			
	B3LYP	2.054	1.662	1.419			
	PW91	2.047	1.650	1.424			
	BPW91	2.054	1.658	1.426			
	B3PW91	2.042	1.649	1.417			
	CASSCF	2.085	1.703	1.415			
$[Be(C_5H_5)_2]/C_s$	RHF	1.920 – 1.935	1.511	1.409 – 1.411	179.2	112.8	– 6.27
		1.763 – 3.365	2.523	1.346 – 1.480			
	B3LYP	1.908 – 1.935	1.497	1.420 – 1.423	176.7	104.4	– 2.52
		1.786 – 3.201	2.389	1.375 – 1.470			
	PW91	1.901 – 1.926	1.502	1.425 – 1.429	172.7	92.0	0.93
		1.777 – 2.951	2.197	1.395 – 1.459			
	BPW91	1.908 – 1.953	1.505	1.427 – 1.431	172.8	94.8	0.57
		1.778 – 3.016	2.247	1.393 – 1.464			
	B3PW91	1.807 – 1.936	1.493	1.417 – 1.421	173.9	96.0	0.63
		1.770 – 3.027	2.259	1.382 – 1.456			
	CASSCF	1.957 – 1.966	1.550	1.416 – 1.417	179.9	113.7	– 9.41
		1.783 – 3.418	2.563	1.359 – 1.491			
$[Be(C_5Me_5)_2]/D_{5d}$	RHF	2.081	1.698	1.414			
	B3LYP	2.069	1.676	1.427			
	PW91	2.062	1.663	1.433			
	BPW91	2.074	1.677	1.435			
	B3PW91	2.059	1.665	1.425			
	CASSCF	2.087	1.701	1.421			
$[Be(C_5Me_5)_2]/C_s$	RHF	1.916 – 1.927	1.500	1.417 – 1.420	179.1	109.0	– 8.53
		1.779 – 3.310	2.487	1.347 – 1.493			
	B3LYP	1.905 – 1.925	1.484	1.429 – 1.433	176.8	102.2	– 3.59
		1.773 – 3.175	2.374	1.378 – 1.484			
	PW91	1.889 – 1.936	1.485	1.435 – 1.439	172.0	92.5	0.04
		1.782 – 2.975	2.217	1.398 – 1.473			
	BPW91	1.928 – 1.938	1.490	1.438 – 1.442	174.8	98.3	– 1.11
		1.788 – 3.111	2.323	1.393 – 1.482			
	B3PW91	1.896 – 1.923	1.478	1.427 – 1.431	175.0	97.7	– 0.70
		1.779 – 3.078	2.300	1.382 – 1.472			
	CASSCF	1.963 – 1.964	1.547	1.422 – 1.425	165.6	87.7	– 3.24
		1.802 – 2.851	2.144	1.384 – 1.466			

[a] For the C_s structures the first line of geometrical parameters r_{BeC}, r_{BeX}, and r_{CC} corresponds to the η^5 ring while the second corresponds to the η^1 ring. [b] X refers to the η^5-ring centroid and X′ to the η^1-ring centroid. [c] Relative energies for the C_s isomer taking the corresponding D_{5d} structure as reference.

wavefunction, reduce the strength of this bond. A slight increase of the Be–(C_5Me_5) separations is observed due to the introduction of the methyl groups indicating that there are only small, if any, steric repulsions between the two bulky C_5Me_5 rings. The computed geometry for $[Be(C_5Me_5)_2]$ is in good agreement with the experimental findings (see Table 2) although the theoretical values for Be–C and Be–(C_5Me_5) separations are a little longer (by 0.02 Å) than the experimentally-determined bond lengths. The floppiness of the molecule and the fact that the experimental values correspond to the solid state, where the packing forces may have a significant influence on the geometry, must be considered when comparing these two sets of theoretical parameters.

The geometries and relative energies computed at different levels of theory for the C_s structures show a few significant differences, indicating that understanding the treatment of electron correlation effects correctly is vital to the interpretation of electronic structure and bonding in these complex systems. All Be–C separations involving the η^5 ring are lower than in the corresponding D_{5d} structure indicating a reinforcement of the delocalized Be–Cp′(η^5) bond. With respect to the geometry of the η^1-ring, an important qualitative difference appears in the coordination mode of the η^1-ring depending on the correlation functional used. For $[Be(C_5H_5)_2]$ the C_σ has a tetrahedral coordination at RHF, CASSCF or B3LYP levels, while the structures predicted by those functionals employing the PW91 correlation functional can be described more as of the slip-sandwich type, with a Be-C_σ-X′ (X′ = (η^1)-ring centroid) angle very close to 90°. This reflects a fundamental difference in the treatment of the electron correlation in this functional that is also present on the computed relative energies. While either the B3LYP functional predicts the C_s to be the lower energy structure (by about 3 kcal mol^{-1}), those functionals employing the PW91 correlation functional give much smaller energy differences between the two isomers, about (or less than) 1 kcal mol^{-1}. This is consistent with the slip-sandwich description of the η^1-ring coordination, producing a very fluxional picture of the structure of these systems. The results given by the CASSCF wavefunction are, however, qualitatively different for $[Be(C_5H_5)_2]$ than for $[Be(C_5Me_5)_2]$. For the former, the structure is of the σ-type, close to the HF description, and the energy difference between the two conformations is larger than at any other theoretical level. For $[Be(C_5Me_5)_2]$ the CASSCF structure is clearly of the slip-sandwich type with an energy difference between the two conformations of only 3.2 kcal mol^{-1}.

The bonding model usually utilized to analyze the metal–ligand interactions in metallocenes correlates the atomic orbitals of the cation (in our case Be^{2+}) with the π MOs of Cp^-.[4a] This is a conceptually simple model that allows us to rationalize the bonding in terms of fully ionic and donor–acceptor interactions between these fragments. At the same time it is a very convenient model because it decomposes the bonding in terms of interactions between closed shell species, and many energy partitioning analyses can be applied in this case. For this purpose we have performed constrained space orbitals variations (CSOV) calculations[31] as implemented in our version of the HONDO program. This analysis decomposes the total interaction between two fragments in terms of a frozen core contribution, referred to as the sum of isolated fragments, and polarization and charge transfer contributions.

The results of the CSOV energy decomposition analysis are presented in Table 4 for RHF and BPW91 wavefunctions. The analysis has also been carried out with the B3LYP functional, but the results were almost identical to those of the BPW91 functional. The main contribution is, in all cases, the frozen core interaction between fragments representative of purely electrostatic attraction. For the D_{5d} structures, this contribution amounts to 65% of the total interaction for $[Be(C_5H_5)_2]$, while the ionicity for $[Be(C_5Me_5)_2]$, following this energy decomposition analysis, is reduced to 58%. It may be argued that this high percentage of purely electrostatic interaction can be, at least in part, a reflection of the choice of highly charged fragments as reference. To check this we have performed a similar analysis taking as reference fragments $BeCp^+$ and Cp^-, the results of which are also shown in Table 4. Indeed, these new results show a reduction of around 15–17% on the ionic interaction between fragments, but the general picture of the bonding is similar, with a high covalent character in the bonding that is larger for $[Be(C_5Me_5)_2]$ than for $[Be(C_5H_5)_2]$.

The breakdown of the non-electrostatic contributions provided by the CSOV method shows that only two contributions are significant: the polarization of the $(Cp^-)_2$ fragment in the presence of Be^{2+} and the partial charge transfer from $(Cp^-)_2$ to Be^{2+}, with any other contribution being less than 0.5 kcal mol^{-1}. Of these two, the polarization of $(Cp^-)_2$ accounts for about two thirds of the covalent energetic contributions to the bonding and it is about 30% larger for $(C_5Me_5^-)_2$ than for $(C_5H_5^-)_2$. This reflects the larger extension of the electronic cloud in the C_5Me_5 ligand and the consequent overlap increase with the orbitals of the Be center. The analysis of the energetic bonding contributions on the C_s structures is similar, but with some significant changes. When the reference fragments are Be^{2+} and $(Cp^-)_2$ there is a reduction of the ionic character of the bonding and a corresponding increase of the $(Cp^-)_2$ polarization. Taking $BeCp^+$ and $Cp^-(\eta^1)$ as reference fragments, an increase in the ionic contribution is observed coupled to a reduction in the $Cp^-(\eta^1)$ to $BeCp^+$ charge transfer energetic contribution. These changes can be interpreted as an increase of the covalent character of the Be–Cp(η^5) bond, propitiated by the shorter Be–Cp separation, while the loss of charge delocalization in the Cp(η^1) ring results in a more ionic and less polarizable Be–Cp(η^1) bond.

To obtain further insight about the structure and bonding in biscyclopentadienyl beryllocene complexes, we have performed some additional theoretical calculations on the $[Be(C_5H_5)(C_5H_4Me)]$ and $[Be(C_5Me_5)(C_5Me_4H)]$ systems. For these studies we have employed the 6–31G(d) basis set and the B3LYP functional. The optimized geometries and relative energies for the stationary points found are summarized in Table 5. From these results a complex picture of the potential energy surface of these systems is found, with many minima (η^5-η^1 structures) connected by a η^5-η^5 structure and with small energy differences. In both cases, the minimum energy η^5-η^1 structure has a Be–C(σ)H bond, while those having a Be–C(σ)Me bond are about 3–4 kcal mol^{-1} less stable. In the $[Be(C_5H_5)(C_5H_4Me])$ complex, a secondary minimum with a Be–CH σ-bond to the carbon atom nearest to that having the Me substituent is found only 0.4 kcal mol^{-1} over the absolute minimum that has the Be–C bond as far as possible from the Me substituent. These results are in agreement with experimental NMR findings that indicate that η^1 geometries in which Be is bonded to the CH of the η^1-ring have an important contribution to the solution structure.

These results can be rationalized in the light of the bonding analysis performed for $[Be(C_5H_5)_2]$ and $[Be(C_5Me_5)_2]$. In the mixed cyclopentadienyl rings (C_5MeH_4 and C_5Me_4H) the ring carbon atoms bonded to Me groups are more polarizable than those bonded to H atoms. Correspondingly, there is a charge

Table 4. CSOV energy decomposition analysis results [kcal mol^{-1}].

	$Be^{+2} + (C_5H_5^-)_2$				$Be^{+2} + (C_5Me_5^-)_2$			
	RHF		BPW91		RHF		BPW91	
	D_{5d}	C_s	D_{5d}	C_s	D_{5d}	C_s	D_{5d}	C_s
frozen core	–546.0	–516.8	–534.7	–507.8	–488.4	–474.4	–468.1	–437.3
$(Cp)_2$ Pol[a]	–182.4	–224.3	–194.8	–219.5	–234.1	–266.7	–247.6	–281.8
$(Cp^-)_2$ to Be^{2+} CT[b]	–79.2	–77.9	–90.4	–86.6	–74.8	–73.1	–88.4	–82.7
Be^{2+} Pol	–0.1	–0.2	–0.4	–0.5	–0.1	–0.2	–0.4	–0.6
Be^{2+} to $(Cp^-)_2$ CT	0.0	0.0	–0.1	–0.1	0.0	0.0	–0.1	–0.1
remaining	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
total	–807.6	–819.2	–820.4	–814.5	–797.2	–814.4	–804.6	–802.5
	$Be(C_5H_5)^+ + (C_5H_5^-)$				$Be(C_5Me^+) + (C_5Me_5^-)$			
	RHF		BPW91		RHF		BPW91	
	D_{5d}	C_s	D_{5d}	C_s	D_{5d}	C_s	D_{5d}	C_s
frozen core	–111.1	–124.6	–107.6	–113.2	–88.8	–114.6	–79.7	–94.9
Cp^- Pol	–36.8	–44.6	–39.3	–41.9	–42.7	–42.9	–43.9	–42.4
Cp^- to $BeCp^+$ CT	–35.8	–24.1	–43.9	–31.3	–33.1	–21.8	–42.3	–28.7
$BeCp^+$ Pol	–20.7	–17.8	–18.0	–15.1	–25.9	–21.3	–24.2	–19.2
$BeCp^+$ to Cp^- CT	–1.0	–0.9	–1.4	–1.3	–1.7	–1.5	–2.7	–2.4
remaining	–1.6	–1.1	–1.4	–1.0	–2.9	–1.9	–3.0	–1.9
total	–206.9	–231.1	–211.6	–203.7	–195.2	–203.4	–195.9	–189.1

[a] Pol = polarization. [b] CT = charge transfer.

Table 5. Calculated main geometrical parameters [Å and °] and relative energies [kcal mol^{-1}] for the complexes [Be(C$_5$H$_5$)(C$_5$MeH$_4$)] and [Be(C$_5$Me$_5$)(C$_5$Me$_4$H)].

Structure	r_{BeC}[a]	r_{BeX}[a]	r_{CC}[a]	$\alpha_{XBeX'}$	$\beta_{BeC1X'}$	E_{rel}
[Be(C$_5$H$_5$)(C$_5$MeH$_4$)]						
η^5-η^5	2.019–2.118	1.675	1.417–1.422	173.3		3.2
	2.002–2.119	1.658	1.420–1.421			
η^5-η^1(Me)	1.907–1.946	1.499	1.420–1.423	153.8	96.4	4.0
	1.775–3.053	2.278	1.381–1.468			
η^5-η^1(H)	1.906–1.930	1.488	1.421–1.423	152.3	107.4	0.4
	1.750–3.266	2.428	1.371–1.481			
η^5-η^1(H)	1.907–1.930	1.489	1.421–1.422	152.8	108.5	0.0
	1.750–3.290	2.450	1.370–1.477			
η^1-η^5	1.910–1.918	1.483	1.421–1.426	151.8	106.0	4.1
	1.758–3.236	2.416	1.374–1.473			
Be(C$_5$Me$_5$)(C$_5$Me$_4$H)						
η^5-η^5	2.051–2.058	1.660	1.426–1.428	179.1		3.9
	2.031–2.094	1.680	1.421–1.430			
η^5-η^1(H)	1.903–1.915	1.475	1.430–1.433	152.9	110.9	0.0
	1.789–3.329	2.489	1.374–1.485			
η^5-η^1(Me)	1.899–1.921	1.476	1.429–1.433	152.3	103.2	3.0
	1.769–3.219	2.389	1.372–1.483			
η^5-η^1(Me)	1.902–1.920	1.478	1.429–1.433	152.2	101.7	4.0
	1.733–3.173	2.366	1.373–1.487			
η^1-η^5	1.886–1.937	1.487	1.425–1.436	153.5	103.7	3.9
	1.770–3.206	2.396	1.376–1.486			

[a] For the η^5-η^1 structures the first line of geometrical parameters (r$_{BeC}$, r$_{BeX}$ and r$_{CC}$) corresponds to the η^5 ring while the second corresponds to the η^1-ring.

localization in the latter, resulting in a stronger Be–CH σ-bond. Thus, those structures where the Be η^1-ring interaction takes place through a Be–CH bond are more stable due to this charge localization on the CH carbon atom. When two of these structures are possible they are nearly degenerate, but with a slight energy balance in favor of that structure having the Me group as far as possible from the Be–C(σ) bond.

Conclusions

At variance with beryllocene, the low-temperature X-ray studies carried out with the methyl-substituted beryllocenes **1**–**3** lead to structures with no positional or thermal disorder. The molecules of **1** and **3** exhibit η^5/η^1 geometries with nearly parallel Cp′ rings, and in both compounds the η^1-C$_5$Me$_4$H ligand binds to Be through the CH carbon atom, possibly to make the strongest possible bond. Theoretical studies on **3** are in agreement with these findings, the preference of Be for binding to the CH group being interpreted as a result of the larger charge localization on this side of the η^1-ring.

Quite unexpectedly, the long-sought [Be(C$_5$Me$_5$)$_2$] (**2**), has an almost regular sandwich structure in the solid state. Although our theoretical calculations indicate a preference for the η^5/η^1 structure, the fact that the solid-state experimental Be–Cp′ centroid length (hence the separation between the rings) is somewhat smaller than the computed value may suggest that the compression resulting from crystal packing effects may create steric repulsion between the ring substituents that distort the molecule toward the η^5/η^5 geometry. This proccess is energetically facile as the energy difference between both structures is very low.

Experimental Section

CAUTION: Beryllium compounds are very toxic by inhalation and in contact with the skin, are irritating to the respiratory system, and present the danger of very serious irreversible effects.

General methods: All preparations and manipulations were carried out under oxygen-free argon using conventional Schlenk techniques. Solvents were rigorously dried and degassed before use. The petroleum used had b.p. 40–60 °C. The complex [Be(η^5-C$_5$Me$_5$)Cl] was prepared according to the literature procedure.[9] Microanalyses were obtained at the Microanalytical Service of the Instituto de Investigaciones Químicas (Sevilla). Infrared spectra were recorded on a Bruker, Vector 22 spectrometer. NMR spectra were recorded on Bruker AMX-300, DRX-400 and DRX-500 spectrometers. The ^{1}H and ^{13}C resonances of the solvent were used as the internal standard, and the chemical shifts are reported relative to TMS. ^{9}Be chemical shifts are referenced to external BeCl$_2$, 0.1 M in D$_2$O.

Compound 1, [Be(C$_5$Me$_4$H)$_2$]: BeCl$_2$ (0.824 g, 10 mmol) and K[C$_5$Me$_4$H] (3.2 g, 20 mmol) were suspended in diethyl ether (200 mL) and stirred overnight at room temperature. Removal of the solvent under vacuum and extraction with petroleum ether afforded crystals of **1** after cooling at −30 °C. Yield 1.76 g, 70 %; m.p. 83 °C; ^{1}H NMR (500 MHz, [D$_8$]toluene, 25 °C): $\delta = 1.79$ (s, 1 H; Cp′CH$_3$), 1.82 (s, 12 H; Cp′CH$_3$), 4.36 ppm (s, 2 H; Cp′CH); ^{13}C NMR (125 MHz, [D$_8$]toluene, 25 °C): $\delta = 10.1$ (s; CH$_3$), 12.4 (s; CH$_3$), 83.0 (s; CH), 117.3 (s; *C*CH$_3$), 117.7 ppm (s; *C*CH$_3$); ^{1}H NMR (500 MHz, [D$_8$]toluene, −90 °C): $\delta = 1.84$ (s, 12 H; Cp′CH$_3$), 1.87 (s, 12 H; Cp′CH$_3$), 4.25 ppm (s, 2 H; Cp′CH); ^{13}C NMR (125 MHz, [D$_8$]toluene, −90 °C): $\delta = 10.6$ (s; CH$_3$), 12.8 (s; CH$_3$), 80.4 (s; CH), 117.8 (s; *C*CH$_3$), 118.7 ppm (s; *C*CH$_3$); ^{9}Be NMR ([D$_6$]benzene, 25 °C): $\delta = -19.9$ ppm ($w_{1/2} = 9.7$ Hz); IR (Nujol): $\tilde{\nu} = 3065$, 2728, 1244, 1040, 798 cm^{-1}; elemental analysis calcd (%) for C$_{18}$H$_{26}$Be: C 86.0, H 10.4; found: C 85.1, H 10.6.

Compound 2, [Be(C$_5$Me$_5$)$_2$]: The synthesis is similar to that of compound **1**. BeCl$_2$ (0.482 g, 6 mmol) and K[C$_5$Me$_5$] (2.088 g, 12 mmol) were stirred for 84 h in a 1:1 mixture of toluene/diethyl ether (80 mL) while the temperature of the heating bath was maintained at 115°C. The solvent was then removed under vacuum and the residue extracted with petroleum ether. Cooling at −30°C overnight gave crystals of **2** in approximately 50 % yield (0.84 g); m.p. 237°C; ^{1}H NMR (400 MHz, [D$_8$]toluene, 25°C): $\delta = 1.81$ ppm (s, 30 H; Cp′CH$_3$); ^{13}C NMR (100 MHz, [D$_8$]toluene, 25 °C): $\delta = 10.4$ ppm (s; CH$_3$), 110.5 (s; *C*CH$_3$); ^{1}H NMR (400 MHz, [D$_8$]toluene, −90 °C): $\delta =$ 1.91 ppm (s, 30 H; Cp′CH$_3$); ^{13}C NMR (100 MHz, [D$_8$]toluene, −90°C): $\delta =$ 10.4 (s; CH$_3$), 109.7 ppm (s; *C*CH$_3$); ^{9}Be NMR ([D$_6$]benzene, 25 °C): $\delta =$ −21.7 ppm ($w_{1/2} = 4.4$ Hz); IR (Nujol): $\tilde{\nu} = 2723$, 1030, 715 cm^{-1}; elemental analysis calcd (%) for C$_{20}$H$_{30}$Be: C 85.9, H 10.8; found: C 85.7, H 10.8.

Compound 3, [Be(C$_5$Me$_5$)(C$_5$Me$_4$H)]: [Be(C$_5$Me$_5$)Cl] (1.35 g, 7.52 mmol) and K[C$_5$Me$_4$H] (1.20 g, 7.52 mmol) were suspended in 100 mL of a 1:1 mixture of toluene/diethyl ether and heated, with stirring, at 115 °C for 84 h. Removal of the solvent under reduced pressure and extraction with petroleum ether, followed by filtration, afforded a clear solution from which colorless crystals of the title compound were collected after concentration and cooling at −30 °C. Yield 1.47 g, 74 %; m.p. 96–99 °C; ^{1}H NMR (400 MHz, [D$_8$]toluene, 25 °C): $\delta = 1.59$ (15 H; C$_5$*Me*$_5$), 1.91 and 1.84 (6 H, 6 H; C$_5$*Me*$_4$H), 3.50 ppm (1 H; C$_5$Me$_4$*H*); ^{13}C NMR (100 MHz, [D$_8$]toluene, 25 °C): $\delta = 9.2$ (C$_5$*Me*$_5$), 11.5 and 14.1 (2 Me, 2 Me; C$_5$*Me*$_4$H), 65.7 (*C*H), 108.9 (*C*$_5$Me$_5$), 123.1 and 125.4 ppm (2 C, 2 C; *C*$_5$Me$_4$H); ^{1}H NMR (400 MHz, [D$_8$]toluene, −90°C): $\delta = 1.55$ (15 H; C$_5$*Me*$_5$), 2.12 and 1.97 (6 H, 6 H; C$_5$*Me*$_4$H), 3.30 ppm (1 H; C$_5$Me$_4$*H*); ^{13}C NMR (100 MHz, [D$_8$]toluene, -90°C): $\delta = 9.4$ (C_5Me_5), 12.2 and 14.7 (2Me, 2Me; C_5Me_4H), 59.3 (CH), 108.7 (C_5Me$_5$) 124.5 and 128.1 ppm (2C, 2C, C_5Me$_4$H); ^{9}Be NMR ([D$_6$]benzene, 25°C): $\delta = -19.7$ ppm ($w_{1/2} = 9.7$ Hz); IR (Nujol): $\tilde{\nu} =$ 2728, 1240, 1043, 887 cm^{-1}; elemental analysis calcd (%) for $C_{19}H_{28}$Be: C 86.0, H 10.5, found: C 84.8, H 10.8.

Computational details: In all cases, except where explicity indicated, we have employed the 6–31G(d,p) atomic basis set for all elements. This basis set, of double-ζ quality and including polarization orbitals on all atoms, is known to give a reasonable description of the atomic electron density. Restricted Hartree–Fock (RHF) and density functional theory (DFT) calculations have been performed by using the Gaussian 98 program suite.[32] Various functionals have been employed, combining Becke's three-parameter hybrid exchange functional,[33] with either the non-local correlation functional of Lee, Yang, and Parr[34] (B3LYP) or the non-local correlation functional of Perdew[35] (B3PW91) and the gradient corrected exchange functional of Perdew[36] with the same non-local correlation functional of Perdew (PW91). While DFT methods are widely used nowadays, these functionals have been developed focusing on systems containing only low Z elements with wavefunctions well aproximated by a single Slater determinant[37]. This imposes some restrictions on functionals derived from KS theory and, recently, it has been suggested that, in cases where quasi-degenerations are present, more than one determinant may be needed to construct the exact energy functional. For these reasons CASSCF calculations have been undertaken to check for possible effects of the non-dynamic correlation in the electronic structure of the complexes studied here. The valence structure of Be(C_5H_5)$_2$ is complex, due to the large number of electrons present. As our goal is to adequately describe the bonding between the Be atom and the two (C_5H_5) rings, the logical choice for the active space includes the valence shell of the Be atom and the π system of both Cp rings. This produces an active space consisting of 12 electrons distributed over 14 molecular orbitals. Given that the last MO in this active space was found in preliminary calculations to be practically empty, we have deleted it from the active space and, finally, kept an active space of 12 electrons distributed over 13 MOs that produces a CI wavefuction of 736164 CSF. This active space is expected to adequately describe near degeneracy effects both intra (C_5H_5) π systems and those resulting from charge transfer between the Be atom and (C_5H_5) rings. Those CASSCF calculations have been undertaken using a locally modified version of the HONDO program system[38] that allows us to perform direct and parallel CI calculations on a Beowulf-type computer.

Crystal structure determinations: Crystals of **1**, **2** and **3** suitable for X-ray studies were obtained by crystalization from petroleum ether (**1** and **2**) and by sublimation under vacuum (**3**). Crystal data and experimental details are given in Table 1. All X-ray data were collected an a Brucker-Siemens Smart CCD diffractometer equipped with a low temperature device and a normal focus, 2.4 kW sealed tube X-ray source (molybdenum radiation, $\lambda = 0.71067$ Å) operating at 50 kV and 20 mA. Data were collected using ω scan ($3 < \theta < 21°$) for **1** (whose crystals exhibited poor quality so there were no reflections over 21°), $2 < \theta < 31°$ for **2** and $2.59 < \theta < 29.67$ for **3**. The structures were solved by direct methods (G. M. Sheldrick, SHELX-92, Program for Crystal Structure Determination, University of Cambridge, **1992**). Hydrogen atoms were located in difference Fourier maps. Refinements were by full-matrix least-squares analysis with anisotropic thermal parameters for all non-hydrogen atoms and isotropic for hydrogen atoms in all cases.

CCDC-137573 (**1**), CCDC-137574 (**2**), and CCDC-193648 (**3**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB21EZ, UK; fax: (+44)1223-336-033; or deposit@ccdc.cam.ac.uk).

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