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Synthesis and X-ray Structures of $[Be(C_5Me_4H)_2]$ and $[Be(C_5Me_5)_2]$[**]

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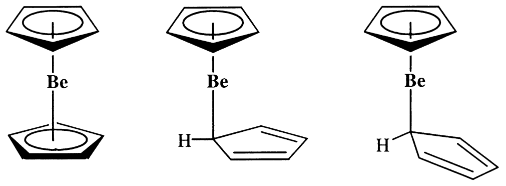
Dedicated to Professor José Elguero

Beryllocene, $[Be(C_5H_5)_2]$, the lightest member of the alkaline earth metallocenes[1] and of the general bis(metallocene) series of compounds $[MCp_2']$, has aroused intense structural debate since its preparation by Fischer and Hofmann in 1959.[2] Structures **I**–**III** are some of the proposed models. Its unexpected dipolar nature[3] is in disagreement with the symmetrical ferrocene-like structure **I**. The most recent X-ray study,[4a] confirmed the slip-sandwich η^5/η^1 structure **II** with disordered Be atoms at −145 °C. This geometry is also in accord with electron diffraction data[5] and with molecular dynamics calculations,[6] and it has been rationalized by Beattie and co-workers, along with the structures displayed by other main-group metal cyclopentadienyls.[7] Very recent density-functional theory (DFT) calculations on structure **I** and **III** concluded that the σ-π structure **III** is lower in energy.[8]



I **II** **III**

Despite this long controversy and the existence of many half-sandwich Be compounds, including $[Be(\eta^5\text{-}C_5Me_5)Cl]$,[9] no other beryllocenes have been reported to date, with the exception of $[Be(\eta^5\text{-}C_5Me_5)(\eta^1\text{-}C_5H_5)]$, which has been characterized only in solution.[10] Related dihydro-1*H*-azaboryl species have also been investigated.[11] Here we present our initial results on the synthesis and solid-state structures of the beryllocenes **1** and **2**.

$[Be(\eta^5\text{-}C_5Me_4H)(\eta^1\text{-}C_5Me_4H)]$ **1**

$[Be(\eta^5\text{-}C_5Me_5)_2]$ **2**

Compound **1** can be synthesized by the simple room-temperature reaction of $BeCl_2$ and $K[C_5Me_4H]$ in diethyl ether [Eq. (1)]. Following crystallization from petroleum ether, **1** can be isolated in about 70% yield in the form of white crystals, soluble in hexane, benzene, and other nonpolar organic solvents. Both solid samples and solutions of **1** exhibit high thermal stability, but the compound is very reactive towards H_2O and O_2 and decomposes immediately in the presence of air. Similar to $[Be(C_5H_5)_2]$,[12] compound **1** is highly fluxional in solution; the two rings are equivalent down to −90 °C according to the ^1H and ^{13}C NMR spectra (C_7D_8; see Experimental Section).

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

Single crystals of **1** suitable for X-ray structure analysis were investigated at −160 °C and were found to be orthorhombic.[13] Figure 1a shows the molecular structure and Figure 1b a schematic representation of the Be–η^1-C_5Me_4H moiety. In contrast to the structure of $[Be(C_5H_5)_2]$, in which the Be atom is disordered between two crystallographically equivalent sites, no positional or thermal disorder appears

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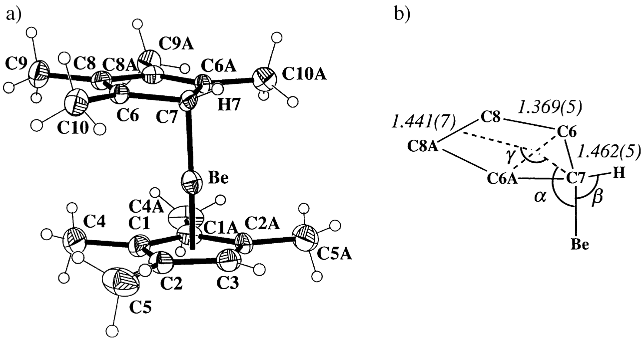

Figure 1. a) Molecular structure of compound **1**. b) Schematic representation of the Be$-\eta^1$-C_5Me_4H moiety of **1**; $\alpha = 100.5(5)$, $\beta = 106(2)$, $\gamma = 173.7(4)^\circ$.

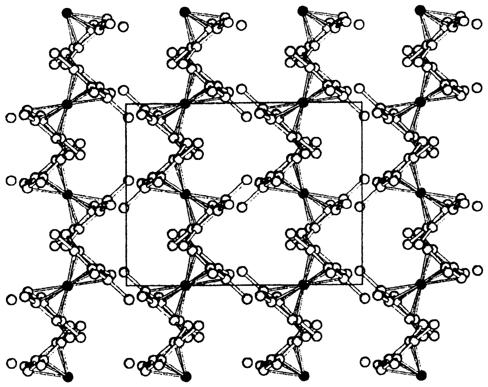

Figure 2. View of the cell of **2** along [100].

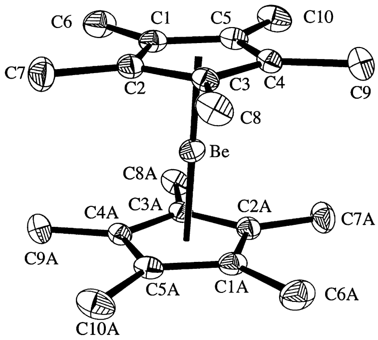

Figure 3. Molecular structure of **2**.

to exist in **1**. The Be atom is coordinated to one η^5-C_5Me_4H ring and to one η^1-C_5Me_4H ring. The distance between Be and the centroid of the former (1.471(7) Å) and its carbon atoms (av. 1.90(7) Å) compare well with those found in $[Be(C_5H_5)_2]$.[4] In the Be$-\eta^1$-C_5Me_4H moiety the Be$-$C7 separation of 1.769(8) Å is in the middle of the range of Be$-$C bonds (1.70–1.85 Å[14]). This ring is not planar. The plane defined by carbon atoms C6, C6A, and C7 forms an angle of 11.7(3)° with the η^5-C_5Me_4H ring, but the best mean plane is almost parallel to the η^5 ring (6.6(1)°). The hydrogen atom H7 deviates by 0.46 Å from the plane of C7 and the adjacent carbons and points away from Be. Altogether these data indicate a geometry around C7 closer to distorted tetrahedral than in $[Be(C_5H_5)_2]$.[4a, 7] In the latter, the σ-bonded carbon is nearly coplanar with the neighboring carbons and the attached hydrogen, hence its geometry has been described as trigonal pyramidal.[4a, 7]

The facile formation of **1** encouraged us to search for a suitable synthesis of the C_5Me_5 analogue, $[Be(C_5Me_5)_2]$, even though the Be center of this complex is thought to be sterically overcrowded.[1] Solid-angle estimations predict the putative $[Be(\eta^5\text{-}C_5H_5)_2]$ species to be a severely congested molecule.[15] Despite this, we have found that $BeCl_2$ and $K[C_5Me_5]$ react slowly (3.5 days) in a mixture of toluene and diethyl ether at 115 °C to give the desired compound **2** at about 50% yield [Eq. (2)]. Similar to compound **1**, $[Be(C_5Me_5)_2]$ **2** is soluble in nonpolar organic solvents and decomposes instantly in the presence of O_2 or H_2O. Its ^1H NMR spectrum merely shows a singlet at $\delta = 1.83$, whereas in the $^{13}C\{^1H\}$ spectrum the ring carbons resonate at $\delta = 110.5$ (20 °C; $\delta = 109.7$ at -90 °C). Since in other Be and Mg compounds containing η^5-C_5Me_5 ligands (for example, $[Be(\eta^5\text{-}C_5Me_5)Cl]$,[9, 10] $[Be(\eta^5\text{-}C_5Me_5)(\eta^1\text{-}C_5H_5)]$,[10] $[Mg(\eta^5\text{-}C_5Me_5)_2]$,[16] among others[14a, 16]) the corresponding signal appears invariably in the very narrow range of $\delta = 110$–108, **2** can be represented as $[Be(\eta^5\text{-}C_5Me_5)_2]$. This proposal has been confirmed by X-ray studies at -160 °C.

$$BeCl_2 + 2\,K[C_5Me_5] \xrightarrow[84\,h]{115\,^\circ C} \underset{\mathbf{2}}{Be(C_5Me_5)_2} + 2\,KCl \qquad (2)$$

Compound **2** forms monoclinic crystals,[13] with four formula units per unit cell (Figure 2). The molecular structure represented in Figure 3 shows that the beryllium atom is bonded to two planar and parallel C_5Me_5 ligands (the average deviation from the mean plane is only 0.01 Å), which are separated by 3.310(1) Å (the interlayer separation in graphite is 3.35 Å).[17] The Be$-$Cp′ centroid separation (1.655(1) Å) and Be$-C_{ring}$ distances are comparable to those found in the related $[Mg(\eta^5\text{-}C_5Me_5)_2]$[18] and $[Al(\eta^5\text{-}C_5Me_5)_2]^+$[19] species after allowance is made for the differences in the radii of the metals (see below). The five Be$-$C distances to the rings in **2** are not identical since they range from 1.969(1) (Be$-$C2) to 2.114(1) Å (Be$-$C5). Consequently, the Be$-$Cp′ centroid vectors are not exactly perpendicular to the rings but form an angle of 87.1(5)°. It is difficult to decide whether these facts are meaningful in terms of Be$-C_5Me_5$ bonding (the similarity between this structure and the η^3/η^3 model[6] suggested for the transition state of the ring inversion mechanism in $[Be(C_5H_5)_2]$ is evident) or are determined by crystal packing effects. Considering the long Be$-C_{ring}$ bonds, we favor the second possibility. A difference of only 11 kJ mol^{-1} has been calculated to exist among several model structures for beryllocene[6] and a compression by 0.02 Å of the metal–ring distances from equilibrium in a compound like $[Mg(\eta^5\text{-}C_5H_5)_2]$ has been estimated to require[20a] only 0.7 kJ mol^{-1}.

The present study on beryllocenes confirms the tendency of the small beryllium atom to adopt an η^5/η^1 slip-sandwich structure in $[BeCp_2']$ compounds. Moreover, it has been unexpectedly revealed for the C_5Me_5 ligand that the η^5/η^5 structure becomes more favorable in the solid state. It thus appears that if one of the Cp′ rings forms a sufficiently strong σ Be$-CH_{ring}$ bond, it prevails over the somewhat weaker

Be—η^5-Cp′ binding and the η^5/η^1 structure is adopted. If the input to the binding energy that arises from the Be-C σ-bond becomes weaker, as expected for Be—η^1-C_5Me_5, the contribution from the delocalization of the ring π-system could prevail,[7] with the result that the [Be(η^5-C_5Me_5)$_2$] structure is preferred. Crystal packing effects may also enforce the symmetric sandwich structure, whereas the alternative slip-sandwich formulation, [Be(η^5-C_5Me_5)(η^1-C_5Me_5)], could be destabilized by van der Waals repulsions between the Me groups of the η^5-C_5Me_5 ring and the Me group on the carbon atom of the η^1-C_5Me_5 ring σ-bonded to beryllium. DFT calculations and gas-phase electron diffraction studies on compound **2**, currently in progress, are expected to clarify some of the above aspects and to provide further relevant information on the bonding and structural properties of **2**. Naturally, bonding in **2** is weaker than in the transition metal metallocene analogues, as attested by the very long Be—C_{ring} separations (recall that Be—C bonds range from 1.70 to 1.85 Å[14]). It appears, however, comparable to that in [Mg(η^5-C_5Me_5)$_2$][18, 20] and [Al(η^5-C_5Me_5)$_2$]$^+$.[19] In the three species, the M—C_{ring} separations amount to 2.05 (**2**, average value), 2.34 (Mg), and 2.16 Å (Al), whilst the effective ionic radii of these metals in six-fold coordination are 0.45 (calculated), 0.72, and 0.535 Å, respectively.[21]

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.

1: $BeCl_2$ (0.824 g, 10 mmol) and K[C_5Me_4H] (3.2 g, 20 mmol) were suspended in diethyl ether (200 mL) and stirred overnight at room temperature. Removal of the solvent in vacuo and extraction with petroleum ether afforded crystals of **1** after cooling to −30 °C. Yield 70%; m.p. 83 °C; ^{1}H NMR (500 MHz, [D$_6$]benzene, 25 °C): $\delta = 1.80$ (s, 12H; Cp′CH$_3$), 1.83 (s, 12H; Cp′CH$_3$), 4.39 (s, 2H; Cp′CH); ^{1}H NMR (400 MHz, [D$_8$]toluene, −90 °C): $\delta = 1.75$ (s, 12H; Cp′CH$_3$), 1.78 (s, 12H; Cp′CH$_3$), 4.14 (s, 2H; Cp′CH); ^{13}C{^{1}H} NMR (125 MHz, [D$_6$]benzene, 25 °C): $\delta = 10.1$ (s, CH$_3$), 12.4 (s, CH$_3$), 82.8 (m, CH), 117.3 (s, *C*CH$_3$), 117.7 (s, *C*CH$_3$); ^{13}C{^{1}H} NMR (100 MHz, [D$_8$]toluene, −90 °C): $\delta = 10.7$ (s, CH$_3$), 13.0 (s, CH$_3$), 79.8 (s, CH), 118.0 (s, *C*CH$_3$), 119.1 (s, *C*CH$_3$); IR (Nujol): $\tilde{\nu} = 3065$ (m), 2728 (w), 1244 (m), 1040 (m), 798 (s) cm^{-1}; elemental analysis calcd. for $C_{18}H_{26}Be$: C 86.0, H 10.4; found C 85.1, H 10.6.

2: The synthesis is similar to that of compound **1**. $BeCl_2$ (0.482 g, 6 mmol) and K[C_5Me_5] (2.088 g, 12 mmol) are stirred for 84 h in a 1:1 mixture of toluene:diethyl ether (80 mL) while the temperature of the heating bath is maintained at 115 °C. The solvent is then removed under vacuum and the residue extracted with petroleum ether. Cooling to −30 °C overnight gives crystals of **2** in ca. 50% yield; m.p. 237 °C; ^{1}H NMR (400 MHz, [D$_6$]benzene, 25 °C): $\delta = 1.83$ (s, 30H, Cp′CH$_3$); ^{13}C{^{1}H} NMR (100 MHz, [D$_6$]benzene, 25 °C): $\delta = 10.4$ (s, CH$_3$), 110.5 (s, *C*CH$_3$); IR (Nujol): $\tilde{\nu} = 2723$ (w), 1030 (m) 715 (s) cm^{-1}; elemental analysis calcd. for $C_{20}H_{30}Be$: C 85.9, H 10.8; found: C 85.7, H 10.8.

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[13] Crystal data for $C_{18}H_{26}Be$ (**1**) and $C_{20}H_{30}Be$ (**2**). The compounds crystallize in the *Pnma* and *C2/c* space groups, respectively, with cell parameters: $a = 12.918(3)$, $b = 15.735(3)$, $c = 7.621(2)$ Å (**1**) and $a = 14.9127(5)$, $b = 11.9919(4)$, $c = 9.4979(3)$ Å, $\beta = 94.839(1)°$ for (**2**). The crystals, with dimensions $0.10 \times 0.20 \times 0.20$ mm^3 (**1**) and $0.35 \times 0.30 \times 0.30$ mm^3 (**2**), were mounted on a Bruker-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 at −160 °C using ω scans ($3 < \theta < 21°$) for **1** (whose crystals exhibited poor quality so there were no reflections over 21°) and $2 < \theta < 31°$ for **2**. The total number of reflections measured was 2661 and 8398 of which 777 and 2450 were considered independent, respectively. The structure was 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 both cases. Final *R* values are $R1 = 0.054$ and 0.053, respectively. Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication nos. CCDC-137573 and -137574. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB21EZ, UK (fax: (+44)1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).

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