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Synthesis and structural characterization of Be(η^5-C_5Me_5)(η^1-C_5Me_4H). Evidence for ring-inversion leading to Be(η^5-C_5Me_4H)(η^1-C_5Me_5)†

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The mixed-ring beryllocene Be(C_5Me_5)(C_5Me_4H), that contains η^5-C_5Me_5 and η^1-C_5Me_4H rings, the latter bonded to the metal through the CH carbon atom (X-ray crystal structure) reacts at room temperature with CNXyl (Xyl = C_6H_3-2,6-Me_2) to give an iminoacyl product, Be(η^5-C_5Me_4H)[C(NXyl)C_5Me_5] derived from the inverted beryllocene structure Be(η^5-C_5Me_4H)(η^1-C_5Me_5).

Apart from Be(C_5Me_5)$_2$ which exhibits in the solid state an almost regular sandwich structure,[1] the two other beryllocenes structurally characterized by X-ray methods, *viz.* Be(C_5H_5)$_2$[2] and Be(C_5Me_4H)$_2$,[1] addopt a slip-sandwich, or $\eta^5/\eta^1(\pi)$, geometry, with two nearly parallel rings. However, in spite of the different coordination of the two cyclopentadienyl ligands,[3] only one set of resonances for the C_5H_5 and C_5Me_4H groups is found in the NMR spectra of the complexes, even at low temperatures (−135 °C).[1,4] Thus beryllocenes are highly fluxional molecules that participate in dynamic processes, very fast on the NMR time scale even at the lowest temperatures accessible.

Molecular dynamic calculations on Be(C_5H_5)$_2$[5] have identified two very facile rearrangements, namely 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 (through an η^5/η^2 transition state; calculated activation barrier of 5 kJ mol^{-1}) and a molecular inversion that interchanges the η^5- and η^1-rings by means of an η^3/η^3 transition state (activation energy 8 kJ mol^{-1}). The rates for molecular redistribution in solution[4b] (300 K) and in the gas phase[5] (400 K) are of the order of 10^{10}–10^{12} s^{-1}, therefore, as indicated above, detection of these processes by NMR methods is unattainable.

We have employed recently the reaction of Be(C_5Me_4H)$_2$ and CNXyl (Xyl = C_6H_3-2,6-Me_2) as a chemical probe[6] for the sigmatropic rearrangement, and demonstrated the existence in solution of η^5/η^1 isomers of octamethyl beryllocene. Naturally, the identity of the two rings makes molecular inversion (if operative) invisible. To circumvert this problem, we have prepared the mixed-ring complex Be(C_5Me_5)(C_5Me_4H) (**1**) and have initiated the study of its reactivity toward CNXyl.

Nonamethylberyllocene (see Fig. 1) can be prepared by the high-temperature interaction of Be(C_5Me_5)Cl[7] and K(C_5Me_4H) [eqn. (1)].

$$\mathrm{Be(C_5Me_5)Cl + K(C_5Me_4H)} \xrightarrow[\text{-KCl}]{115\ °\mathrm{C},\ 36\ \mathrm{h}} \mathrm{Be(C_5Me_5)(C_5Me_4H)} \qquad (1)$$

Prolonged heating at elevated temperatures is needed and the reaction gives low isolated yields of the desired beryllocene (*ca.* 25%). Compound **1** is, however, a highly crystalline material that has solubility and other properties similar to those of Be(C_5Me_5)$_2$ and Be(C_5Me_4H)$_2$. A related mixed-ring derivative, Be(C_5Me_5)(C_5H_5) was reported by Aroney and coworkers[7b] and formulated as Be(η^5-C_5Me_5)(η^1-C_5H_5) on the basis of solution IR and NMR spectroscopic studies. Nonetheless, solid-state characterization of this species was not provided.

Crystals of **1** have been studied at low-temperature (130 K) by X-ray methods.‡ In accord with expectations, the C_5Me_5 ring is centrally bound to beryllium (Fig. 1) and the C_5Me_4H group bonded in an η^1-fashion through the CH carbon, C(11). The two rings are planar and nearly parallel [angle of 4.9(1)°]. Metal coordination to the η^5-ring is remarkably regular, the five Be–C distances are almost identical and cluster in the very narrow interval from 1.896(3)–1.919(3) Å. The Be–η^1-C_5Me_4H moiety is characterized by a Be–C(11) distance of 1.776(3) Å and a Be–C(11)-ring plane angle of 102.5°. The difference in the length of the $C_{\beta\beta}$ and $C_{\alpha\beta}$ bonds of only 0.06 Å (α and β refer to the position with respect to the Be-bonded C11 carbon) is suggestive of considerable electron delocalization in the ring π-system.[5] All these data are indicative of a slipped sandwich structure similar to that of Be(C_5H_5)$_2$[2] and Be(C_5Me_4H)$_2$,[1] but with a geometry around C(11) closer to distorted tetrahedral than in Be(C_5H_5)$_2$.

Even if variable temperature ^{1}H and ^{13}C{^{1}H} NMR studies on **1** (from −90 to +95 °C) are indicative of fluxional behaviour, they provide no evidence as for the nature of the processes that occur in solution. The signals due to the ring carbon nuclei of the C_5Me_5 group vary very little with temperature (20 °C, δ 108.9; −90 °C, δ 108.7). Contrarily, the resonance attributable to the CH carbon of C_5Me_4H displaces toward higher field by almost 9 ppm upon lowering the temperature from +95 °C (δ 67.0) to −90 °C (δ 59.3). Parallel changes, albeit of smaller magnitude and opposite direction (*i.e.* to lower field), are registered for the signals associated with the other carbon nuclei

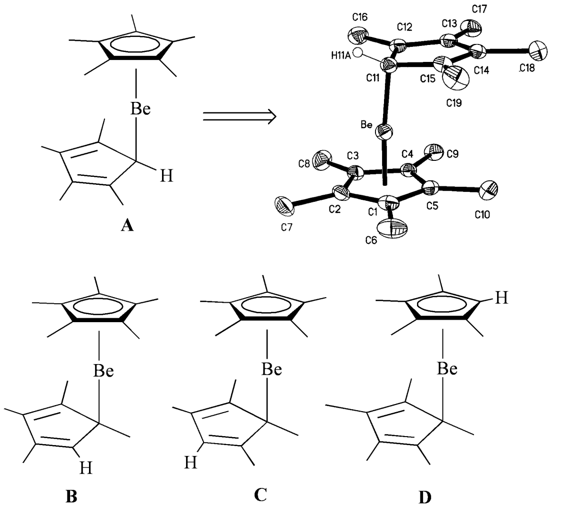

Fig. 1 Isomeric η^5/η^1 structures for Be(C_5Me_5)(C_5Me_4H).

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† Electronic supplementary information (ESI) available: experimental and characterization data for **1** and **2**, computational details. See http://www.rsc.org/suppdata/cc/b2/b208972f/

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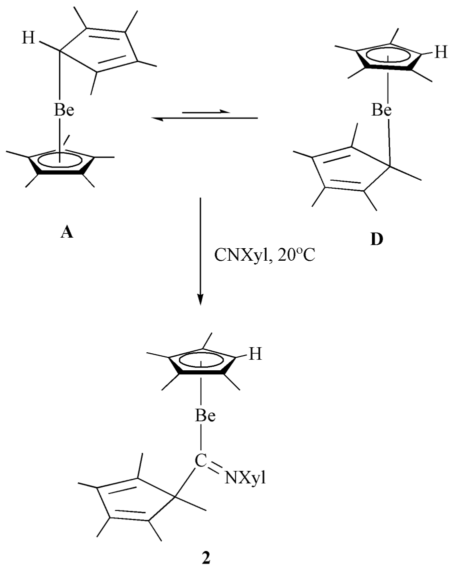
of this ring (δ 124.2 and 122.5, at −95 °C; δ 128.1 and 124.5 at −90 °C, signals due to the α- and β-C nuclei at either of the above temperatures). An important contribution of the Be(η^5-C_5Me_5)(η^1-C_5Me_4H) structure **A** to the solution structure may be inferred from these data. This assumption finds further support in the observation in the $^{13}C\{^1H\}$ NMR spectrum of **1** recorded at +95 °C of a well-resolved coupling (*ca.* 10 Hz) between the quadrupolar ^9Be (I = 3/2) and the ^{13}C nucleus of the CH group. A reasonable explanation for this dynamic behaviour is a sigmatropic shift of the Be(η^5-C_5Me_5) unit around the periphery of the η^1-C_5Me_4H ring. Nevertheless, since the effect of the inverted structure, Be(η^5-C_5Me_4H)(η^1-C_5Me_5), **D** on the observed ^1H and $^{13}C\{^1H\}$ chemical shifts cannot be predicted, concomitant rearrangement of **1** by molecular inversion should not ruled out.

To gain further information on the dynamics of **1**, and in particular to verify the accessibility of the inverted structure **D**, we have investigated the reaction of **1** and CNXyl. Similarly to Be(C_5Me_5)$_2$ and Be(C_5Me_4H)$_2$,[6] stirring at room temperature a solution of Be(C_5Me_5)(C_5Me_4H) and CNXyl allows the formation of an iminoacyl product, **2**. The Be-iminoacyl linkage of **2** is characterized by a sharp IR absorption at 1570 cm^{-1} and by a low-field $^{13}C\{^1H\}$ resonance at δ 156.5 due to the beryllium-bound iminoacyl carbon. However, most remarkably, the analysis of the NMR data (ESI) unambiguosly reveals that **2** contains an η^5-C_5Me_4H ligand, and an iminoacyl functionality that incorporates the C_5Me_5 group of **1** (Scheme 1). In accord with this, three ^{13}C resonances are identified for the C_5Me_4H group at δ 100.6 (CH, $^1J_{CH}$ 165 Hz), 109.6 and 111.2, and another three for those of the C_5Me_5 ring (δ 71.2, 135.6 and 140.6). For the latter, three $^{13}C\{^1H\}$ methyl resonances (δ 11.0, 11.5 and 16.6) can also be discerned. Structural confirmation by X-ray crystallography has been obtained and will be reported elsewhere. Not unexpectedly, the overall structure of **2** is similar to that reported recently for the related beryllium iminoacyl Be(η^5-C_5Me_5)(C(NXyl)C_5Me_5).[6]

Considering that four η^5/η^1 isomers are posible for compound **1**, other isomers of the iminoacyl **2** are likely to exist. However, leaving this aside for the time being, it is worth pointing out that the reaction of Scheme 1 constitutes a chemical demostration of the molecular inversion rearrangement between the non-degenerate structures **A** and **D**.

The electronic structure of the η^5/η^1 isomers of **1** (Fig. 1) has been evaluated with the aid of DFT calculations (see ESI for details†). Naturally, **A** has been found to be the most stable isomer, **B**–**D** lying 3.0–4.0 kcal mol^{-1} higher in energy. The Be–C bond lengths of **A** have been reproduced very accurately (calculated and observed Be–C bond distances are identical). However, and analogously to Be(C_5H_5)$_2$,[9] theory leads to non-parallel rings for **A** (Be–CH-ring plane angle of 111°, experimental value 102.5°), and therefore to a structure close to $\eta^5/\eta^1(\sigma)$, so far demonstrated only in the B(C_5Me_5)$^+$ cation.[10] Differently, when beryllium is η^1-bonded to a CMe group (as in **B**–**D**), calculations lead to the slip-sandwich geometry, with Be–C(Me)-ring plane angles (102–104°) that resemble those experimentally found for beryllocenes[1,2] and zincocenes.[11] The small energy difference among the isomeric structures **A**–**D** provides a theoretical basis for the isolation of the iminoacyl compound **2** and suggests moreover that, like for Be-(C_5Me_4H)$_2$,[6] isolation of other iminoacyl isomers may be feasible.



Scheme 1

In summary, with the X-ray study of **1** the number of structurally characterized beryllocenes has been raised to four.[1,2] Nonamethylberyllocene, Be(η^5-C_5Me_5)(η^1-C_5Me_4H), is however unique among this small family of metallocenes, since it is the only one containing two different cyclopentadienyl rings. Its room temperature reaction with CNXyl yields an iminoacyl product that derives from the inverted beryllocene, Be(η^5-C_5Me_4H)(η^1-C_5Me_5), thereby providing chemical evidence for the molecular inversion process that exchanges the two Cp' groups, of these metallocenes.

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Notes and references

‡ *Crystal data for* **1**: $C_{19}H_{28}Be$, M = 265.42, monoclinic $P2_1/n$, a = 8.0745(5), b = 6.6634(6), c = 30.295(2) Å, β = 92.097(2)°, V = 1628.9(2) Å^3, Z = 4, D_c = 1.082 Mg m^{-3}, T = 130(2) K, total reflections = 6690, unique reflections = 3033 (R_{int} = 0,0385). Final R_1 = 0.084, wR_2 = 0.175 (all data), GoF = 0.93. CCDC reference number 193648. See http://www.rsc.org/suppdata/cc/b2/b208972f/ for crystallographic data in CIF or other electronic format.

1 M. M. Conejo, R. Fernández, E. Gutiérrez-Puebla, A. Monge, C. Ruiz and E. Carmona, *Angew. Chem., Int. Ed.*, 2000, **39**, 1949.

2 (*a*) K. W. Nugent, J. K. Beattie, T. W. Hambley and M. R. Snow, *Aust. J. Chem.*, 1984, **37**, 1601; (*b*) C. H. Wong, T. Y. Lee, K. J. Chao and S. Lee, *Acta Crystallogr., Sect. B*, 1972, **28**, 1662; (*c*) C. H. Wong, T. Y. Lee, T. J. Lee, T. W. Chang and C. S. Liu, *Inorg. Nucl. Chem. Lett.*, 1973, **9**, 667.

3 (*a*) P. Jutzi and N. Burford in *Metallocenes*, ed. A. Togni and R. L. Halterman, Wiley-VCH, **vol. 1**, 1998, ch. 2; (*b*) T. P. Hanusa, *Organometallics*, 2002, **21**, 2559.

4 (*a*) C. Wong and S. Wang, *Inorg. Nucl. Chem. Lett.*, 1975, **11**, 677; (*b*) K. W. Nugent, J. K. Beattie and L. D. Field, *J. Phys. Chem.*, 1989, **93**, 5371.

5 P. Margl, K. Schwarz and P. E. Blöchl, *J. Chem. Phys.*, 1995, **103**, 683.

6 M. M. Conejo, R. Fernández, E. Carmona, E. Gutiérrez-Puebla and A. Monge, *Organometallics*, 2001, **20**, 2434.

7 (*a*) C. J. Burns and R. A. Andersen, *J. Organomet. Chem.*, 1987, **325**, 31; (*b*) S. J. Pratten, M. K. Cooper and M. J. Aroney, *J. Organomet. Chem.*, 1990, **381**, 147.

8 (*a*) J. K. Beattie and K. W. Nugent, *Inorg. Chim. Acta*, 1992, **198–200**, 309; (*b*) L. Nyulászi and P. von Ragué Schleyer, *J. Am. Chem. Soc.*, 1999, **121**, 6872.

9 L. W. Mire, S. D. Wheeler, E. Wagenseller and D. S. Marynick, *Organometallics*, 1998, **37**, 3099.

10 (*a*) A. Voigt, S. Filipponi, C. L. B. Macdonald, J. D. Gorden and A. H. Cowley, *Chem. Comm.*, 2000, 911; (*b*) P. Jutzi and A. Senfert, *J. Organomet. Chem.*, 1978, **161**, 5.

11 (*a*) D. J. Burkey and T. P. Hanusa, *J. Organomet. Chem.*, 1996, **512**, 165; (*b*) B. Fischer, P. Wijkens, J. Boersma, G. van Koten, W. J. J. Smeets, L. Spek and P. H. M. Budzelaar, *J. Organomet. Chem.*, 1989, **376**, 223.

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