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Iminoacylberyllium Compounds Derived from Octamethyl- and Decamethylberyllocene and 2,6-Dimethylphenyl Isocyanide. Evidence for the Existence of η^5/η^1 Isomers of Beryllocenes

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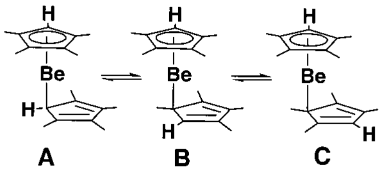
Summary: The existence in solution of η^5/η^1 isomers of the beryllocenes $Be(C_5Me_5)_2$ and $Be(C_5Me_4H)_2$ is inferred from the results of their reaction with CNXyl to give iminoacyl products. The process is reversible and involves coupling of a Be−η^1-Cp′ group with the isocyanide.

Since its preparation in 1959,[1] beryllocene, $Be(C_5H_5)_2$, has attracted considerable attention due to the unusual, nonsymmetric η^5/η^1 structure it possesses in the solid state.[2,3] Recently, we reported the synthesis and solid-state structure of two new beryllocenes, $Be(C_5Me_5)_2$ (**1**) and $Be(C_5Me_4H)_2$ (**2**). In the solid state, molecules of the latter also exhibit an η^5/η^1 structure, whereas those of the former contain two η^5-C_5Me_5 rings.[4]

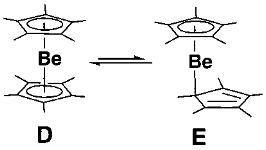
Beryllocene is a highly fluxional molecule,[5] whose dynamic behavior has been explained as involving two very facile processes, namely ring exchange and a sigmatropic shift around the η^1 ring.[5,6] For octamethylberyllocene (**2**) ring exchange also causes the two C_5Me_4H rings to be indistinguishable in the ^1H and $^{13}C\{^1H\}$ NMR spectra, down to −90 °C.[4] However, while in $Be(C_5H_5)_2$ the sigmatropic shift exchanges degenerate structures, in $Be(C_5Me_4H)_2$ this dynamic process would interconvert the isomeric structures **A**−**C**, depicted in Scheme 1, which are not degenerate.

With regard to $Be(C_5Me_5)_2$, a $^{13}C\{^1H\}$ resonance at 110.5 ppm due to the ring carbons was observed at 20 °C, and this resonance shifted slightly to higher field (δ 109.7) upon cooling to −90 °C. Known compounds with a Be(η^5-C_5Me_5) unit[7,8] give the corresponding signal in the very narrow range δ 110−108; hence, it is tempting to propose that the solution structure of **1** is represented by the η^5/η^5 structure found for the molecules of this compound in the solid state. Nevertheless, as $Be(C_5H_5)_2$ and $Be(C_5Me_4H)_2$ have η^5/η^1 structures and molecular dynamic calculations for the former point to a very small energy difference of 11 kJ mol^{-1} between the ground-state η^5/η^1 and the higher energy η^5/η^5 D_{5d} structures,[6] it is reasonable to suggest a fast equilibrium between the isomeric structures **D** and **E**, represented in Scheme 2, exists in solutions of **1**. The NMR data do not allow such a distinction to be made.[4] Accordingly, we have gathered corroborating chemical evidence, and this is presented herein.

Scheme 1. η^5/η^1 Isomers of $Be(C_5Me_4H)_2$



Scheme 2. Isomeric Structures for $Be(C_5Me_4H)_2$



Even though formal insertions of carbon monoxide and organic isocyanides into transition-metal−η^1-Cp′ bonds are not common transformations, examples exist for both CO[9] and CNR.[10] Neither of the beryllocenes **1** and **2** appear to give an adduct or an acyl product upon reaction with CO,[11] even under forcing conditions (100 atm in the case of **2**). Nevertheless, the addition of 1 mol equiv of CNXyl (Xyl = C_6H_3-2,6-Me_2) to solutions

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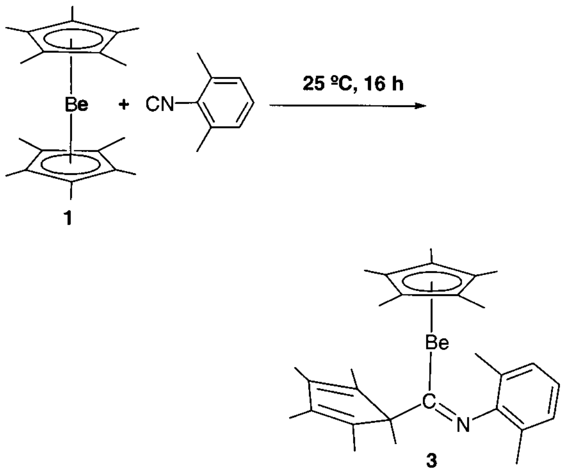
of **1** at room temperature (eq 1) produces the iminoacyl



(1)

complex **3** in 70% isolated yield (at −78 °C the reaction seems to be very slow). The C−C coupling could involve the η^5/η^1 isomer of **1**, i.e., **E**, but as already noted there is no experimental indication for its existence in the solutions of $Be(C_5Me_5)_2$. However, compelling evidence in favor of this proposal derives from studies of a closely related metallocene. Thus, since the isovalent $Zn(C_5Me_5)_2$ has a slip-sandwich η^5/η^1 structure,[12] we studied its interaction with CNXyl and obtained a related iminoacyl, $Zn(\eta^5\text{-}C_5Me_5)(C(NXyl)C_5Me_5)$, with spectroscopic properties similar to those of **3**.[13]

IR and NMR data for **3** are in accord with the formulation proposed. The Be−η^1-iminoacyl linkage is characterized by a sharp IR absorption at 1570 cm^{-1} and by a low-field $^{13}C\{^1H\}$ resonance at δ 155.7 due to the beryllium-bound iminoacyl carbon. Room-temperature ^1H and $^{13}C\{^1H\}$ NMR studies give no indication of reversibility, but at higher temperatures partial dissociation of **3** into **1** and CNXyl is observed. Figure 1 is a van't Hoff plot for the dissociation process in the temperature range from 80 to 115 °C.

Compound **3** has been characterized additionally by low-temperature (−130 °C) X-ray studies, the results of which are summarized in Figure 2.[14] As expected, the Be−Cp′ centroid distance in **3** (1.472 Å) is appreciably shorter than in the parent compound **1** (1.655 Å), doubtless as a reflection of a stronger Be−C_5Me_5 electronic interaction and of a reduced steric strain.

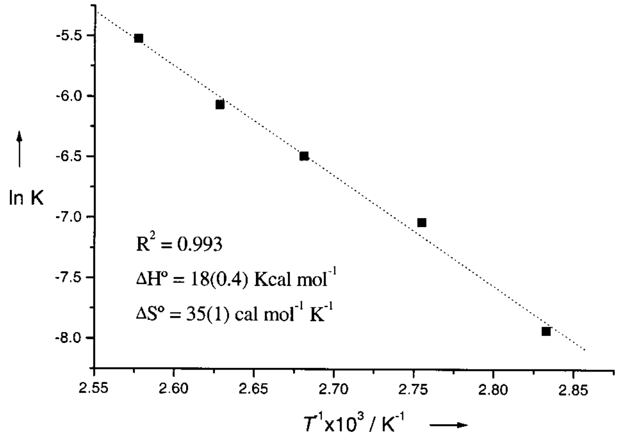


Figure 1. van't Hoff plot for the dissociation process of **3**.

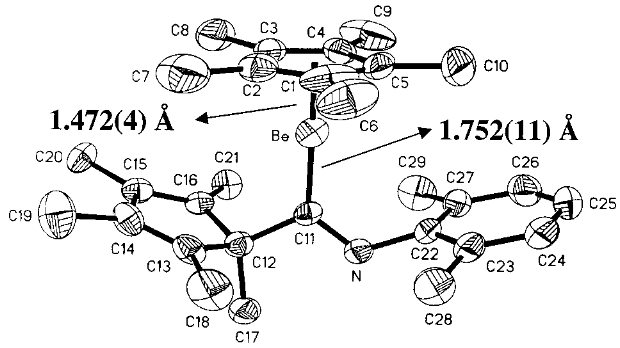
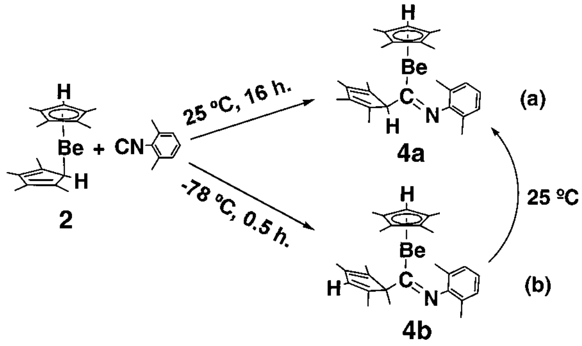


Figure 2. Molecular structure of compound **3**.

Scheme 3. Reaction of 2 with CNXyl



The analogous reaction of **2** and CNXyl gives the iminoacyl compound **4a** (Scheme 3a). ^1H and $^{13}C\{^1H\}$ NMR data are in complete agreement with the proposed structure (see the experimental data below). In addition, the iminoacyl ligand is characterized by a $\nu(C{=}N)$ value of 1560 cm^{-1}. Obviously, complex **4a** derives from the coupling of CNXyl with the Be−C_σ bound of isomer **A** of octamethylberyllocene. At variance with this room-temperature reaction and isolation result, conducting the reaction at −78 °C (Scheme 3b) generates cleanly the iminoacyl isomer **4b** in 68% isolated yield. Once again, ^1H and $^{13}C\{^1H\}$ NMR data (see the experimental data below) for isomer **4b** are in accord with the proposed formulation and indicate it is the iminoacyl derived from isomer **C** of $Be(C_5Me_4H)_2$: i.e., the product of the coupling of the isocyanide carbon with one of the C(Me) carbons in a position β with respect to the CH unit.

As an isolated solid, compound **4b** is stable at room temperature. However, when its solutions are prepared at −78 °C and warmed to room temperature, spectroscopic monitoring reveals a clean conversion to **4a**. At −30 °C, small amounts of another product are detected, since an olefinic ^1H resonance can be discerned at δ 5.69 (the corresponding resonance in **4b** appears at δ 5.78). While it is tempting to propose that this signal corresponds to the missing iminoacyl isomer (i.e., that

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[11] For the analogous reaction of $Ca(C_5Me_5)_2$ and CO see: Selg, P.; Brintzinger, H. H.; Andersen, R. A.; Horvath, I. T. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 791.

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[14] Crystal data for $C_{29}H_{39}BeN$ (**3**). The compound crystallizes in the $P1$ space group, with cell parameters $a = 8.6728(7)$ Å, $b = 16.751(2)$ Å, $c = 18.357(2)$ Å, $\alpha = 99.5050(10)°$, $\beta = 103.4820(10)°$, and $\gamma = 90.4370(10)°$.

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resulting from the coupling to CNXyl of one of the two α-*C*Me atoms), the concentration of the complex remains too low (<5%) to allow its unequivocal characterization.

The fast formation of **4b** at −78 °C implies that structure **C** is sufficiently populated at this temperature. It also indicates that the Be−C(Me) bond of structure **C** undergoes coupling with CNXyl at a faster rate than the Be−C(H) bond of **A**, perhaps as a reflection of the difference in the strength of the two Be−C bonds. It is actually well-established that the stability of alkyl ligands decreases in the order primary > secondary ≫ tertiary, to the point that observable tertiary complexes are rare.[15]

The reaction of beryllocenes **1** and **2** with CNXyl to form the iminoacyls **3** and **4a**,**b** resembles closely the analogous addition of organolithium and organomagnesium reagents to isonitriles to give the corresponding metalloimines, which are useful synthetic reagents.[16] Present data suggest that the reaction may proceed by direct attack of CNXyl onto the polar, relatively weak Be−η^1-Cp′ bond, with formation of a cyclic three-center Be−C(NXyl)−Cp′ transition state. The traditional mechanism, a formal migratory insertion, cannot be completely ruled out. However, as beryllocenes **1** and **2** are sterically congested molecules and furthermore the metal has only the 2s and 2p valence orbitals available, the coordination of the isocyanide prior to migration of the η^1-Cp′ group would require a change in the hapticity of the η^5 ring.[17] Since stronger nucleophiles such as 1,3,4,5-tetramethylimidazol-2-ylidene and pyridine do not react with **1** (80 °C), and moreover Be(η^5-C_5Me_5)(CH_3)[18] is recovered unaltered after treatment with CNXyl (80 °C, 24 h), such a coordination change seems unlikely. Kinetic and mechanistic studies aimed at clarifying these questions are in progress. Nevertheless, and regardless of the precise mechanistic details, the isolation of iminoacyls **3** and **4a**,**b** provide direct experimental evidence for the existence of the η^5/η^1 beryllocene isomers represented in Schemes 1 and 2.

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.

3. Be(C_5Me_5)$_2$ (**1**; 0.279 g, 1 mmol) and CNXyl (Xyl = C_6H_3-2,6-Me_2; 0.131 g, 1 mmol) were dissolved in petroleum ether (30 mL), and the mixture was stirred overnight at room temperature. Removal of the solvent in vacuo and extraction with petroleum ether afforded crystals of **3** after cooling at −30 °C, in 73% isolated yield. Selected data are as follows. ^{1}H NMR (500 MHz, [D_6]benzene, 25 °C, TMS): δ 1.40 (s, 3 H; C(NXyl)-C_5*Me*$_5$), 1.44 (s, 15 H; η^5-C_5*Me*$_5$), 1.73 (s, 6 H, C(NXyl)C_5*Me*$_5$), 1.83 (s, 6 H, C(NXyl)C_5*Me*$_5$). ^{13}C{^{1}H} NMR (125 MHz, [D_6]-benzene, 25 °C, TMS): δ 8.7 (s, η^5-C_5*Me*$_5$), 11.1 (s, C(NXyl)-C_5*Me*$_5$), 11.6 (s, C(NXyl)C_5*Me*$_5$), 18.8 (s, C(NXyl)C_5*Me*$_5$), 71.7 (s, C(NXyl)*C*$_5$Me$_5$), 108.8 (s, η^5-*C*$_5$Me$_5$), 135.2 (s, C(NXyl)*C*$_5$-Me$_5$), 140.7 (s, C(NXyl)*C*$_5$Me$_5$), 155.7 (s, *C*=N). IR (Nujol): ν 1571 (C=N), 1200, 1090, 1065, 826, 758 cm^{-1}. Anal. Calcd for $C_{29}H_{39}NBe$: C, 84.9; H, 9.5; N, 3.4. Found: C, 84.8; H, 9.6; N, 3.4.

4a. The synthesis is similar to that of compound **3**. **4a** was obtained in 68% isolated yield. Selected data are as follows. ^{1}H NMR (400 MHz, [D_6]benzene, 25 °C, TMS): δ 1.36 (s, 6 H, η^5-C_5*Me*$_4$H), 1.55 (s, 6 H, η^5-C_5*Me*$_4$H), 1.77 (s, 6 H, C(NXyl)-C_5*Me*$_4$H), 1.86 (s, 6 H, C(NXyl)C_5*Me*$_4$H), 3.96 (s, 1 H, C(NXyl)-C_5Me$_4$*H*), 4.69 (s, 1 H, η^5-C_5Me$_4$*H*). ^{13}C{^{1}H} NMR (125 MHz, [D_6]benzene, 25 °C, TMS): δ 8.8 (s, η^5-C_5*Me*$_4$H), 10.9 (s, η^5-C_5*Me*$_4$H), 11.6 (s, C(NXyl)C_5*Me*$_4$H), 13.3 (s, C(NXyl)C_5*Me*$_4$H), 77.2 (s, C(NXyl)*C*$_5$Me$_4$*H*), 100.4 (s, η^5-*C*$_5$Me$_4$*H*), 110.2 (s, η^5-*C*$_5$Me$_4$H), 111.5 (s, η^5-*C*$_5$Me$_4$H), 134.6 (s, C(NXyl)*C*$_5$Me$_4$H), 137.3 (s, C(NXyl)*C*$_5$Me$_4$H), 156.7 (s, *C*=N). IR (Nujol): ν 2726, 1643, 1560 (C=N), 1200, 1087, 1033, 884, 774 cm^{-1}. Anal. Calcd for $C_{27}H_{35}NBe$: C, 84.8; H, 9.2; N, 3.7. Found: C, 85.0; H, 9.2; N, 3.7.

4b. The synthesis is similar to that of compounds **3** and **4a**, but the reaction is conducted at −78 °C for 30 min, the solvent removed at ca. −20 °C, and the residue extracted with petroleum ether and crystallized at the same temperature. **4b** was obtained in 55% isolated yield. Selected data are as follows. ^{1}H NMR (400 MHz, [D_8]toluene, −78 °C, TMS): δ 1.24 (s, 3 H, η^5-C_5*Me*$_4$H), 1.25 (s, 3 H, η^5-C_5*Me*$_4$H), 1.53 (s, 3 H, η^5-C_5*Me*$_4$H), 1.55 (s, 3 H, η^5-C_5*Me*$_4$H), 1.57 (s, 3 H, C(NXyl)-C_5*Me*$_4$H), 1.67 (s, 3 H, C(NXyl)C_5*Me*$_4$H), 1.74 (s, 3 H, C(NXyl)-C_5*Me*$_4$H), 1.80 (s, 3 H, C(NXyl)C_5*Me*$_4$H), 4.65 (s, 1 H, η^5-C_5Me$_4$*H*), 5.78 (s, 1 H, C(NXyl)C_5Me$_4$*H*). ^{13}C{^{1}H} NMR (125 MHz, [D_8]toluene, −78 °C, TMS): δ 8.9 (s, η^5-C_5*Me*$_4$H), 11.1 (s, η^5-C_5*Me*$_4$H), 11.3 (s, C(NXyl)C_5*Me*$_4$H), 13.4 (s, C(NXyl)-C_5*Me*$_4$H), 14.2 (s, C(NXyl)C_5*Me*$_4$H), 16.7 (s, C(NXyl)C_5*Me*$_4$H), 71.8 (s, C(NXyl)*C*$_5$Me$_4$H), 101.5 (s, η^5-*C*$_5$Me$_4$*H*), 109.5 (s, η^5-*C*$_5$Me$_4$H), 109.7 (s, η^5-*C*$_5$Me$_4$H), 111.2 (s, η^5-*C*$_5$Me$_4$H), 111.5 (s, η^5-*C*$_5$Me$_4$H), 131.4 (s, C(NXyl)*C*$_5$Me$_4$H), 134.1 (s, C(NXyl)*C*$_5$-Me$_4$H), 141.3 (s, C(NXyl)*C*$_5$Me$_4$H), 148.6 (s, C(NXyl)*C*$_5$Me$_4$H), 156.5 (s, *C*=N). IR(Nujol): ν 2725, 1652, 1560 (C=N), 1200, 1089, 1032, 886, 757 cm^{-1}. Anal. Calcd for $C_{27}H_{35}NBe$: C, 84.8; H, 9.2; N, 3.7. Found: C, 84.7; H, 9.8; N, 3.7.

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Supporting Information Available: Tables giving atomic and thermal parameters and all bond distances and angles for **3**. This material is available free of charge via the Internet at http://pubs.acs.org.

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(15) The crystal, with dimensions (in mm) 0.20 × 0.20 × 0.25, was mounted on 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, λ = 0.710 67 Å) operating at 50 kV and 20 mA. Data were collected at 143(2) K using ω scans over the range 2.68 < θ < 20.81°. The total number of reflections measured was 7641 of which 5049 were considered independent. The structure was solved by direct methods (Sheldrick, G. M. SHELX-86, 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 parameters for hydrogen atoms in both cases. The final *R* value is R1 = 0.1. Crystallographic data for the structure reported in this paper have been deposited with the Cambridge Crystallographic Data Center as supplementary publication no. CCDC-151965.

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