Synthetic, Reactivity, and Structural Studies on Half-Sandwich (η^5-C_5Me_5)Be and Related Compounds: Halide, Alkyl, and Iminoacyl Derivatives

M. del Mar Conejo,[a] Rafael Fernández,[a] Ernesto Carmona,*[a] Richard A. Andersen,*[b] Enrique Gutiérrez-Puebla,*[c] and M. Angeles Monge[c]

Dedicated to Professor G. E. Coates, the pioneer of organoberyllium chemistry, on the occasion of his 86th birthday

Abstract: The half-sandwich compounds [(η^5-C_5Me_5)BeX] (X = Cl, **1a**; Br, **1b**), readily prepared from the reaction of the halides BeX_2 and M[C_5Me_5] (M = Na or K), are useful synthons for other (η^5-C_5Me_5)Be organometallic compounds, including the alkyl derivatives [(η^5-C_5Me_5)BeR] (R = Me, **2a**; CMe_3, **2b**; CH_2CMe_3, **2c**; CH_2Ph, **2d**). The latter compounds can be obtained by metathetical exchange of the halides **1** with the corresponding lithium reagent and exhibit NMR signals and other properties in accord with the proposed formulation. Attempts to make [(η^5-C_5Me_5)BeH] have proved fruitless, probably due to instability of the hydride toward disproportionation into [Be(C_5Me_5)$_2$] and BeH_2. The half-sandwich iminoacyl [(η^5-C_5Me_5)Be(C(NXyl)Cp′)] and [(η^5-C_5Me_4H)Be(C(NXyl)Cp′)][3, 6] where Xyl = C_6H_3-2,6-Me_2 and Cp′ = C_5Me_5 or C_5Me_4H, are formed when the beryllocenes [Be(C_5Me_5)$_2$], [Be(C_5Me_4H)$_2$], and [Be(C_5Me_5)(C_5Me_4H)] are allowed to react with CNXyl. Isolation of three different iminoacyl isomers from the reaction of the mixed-ring beryllocene [(η^5-C_5Me_5)Be(η^1-C_5Me_4H)] and CNXyl, namely compounds **5a**, **5b**, and **6**, provides compelling evidence for the existence in solution of different beryllocene isomers, generated in the course of two very facile processes that explain the solution dynamics of these metallocenes, that is the 1,5-sigmatropic shift of the Be(η^5-Cp′) unit around the periphery of the η^1-Cp′ ring, and the molecular inversion rearrangement that exchanges the roles of the two rings.

Keywords: beryllium · cyclopentadienyl ligands · half-sandwich complexes · iminoacyls · sigmatropic rearrangements

Introduction

In contrast to the many known organoberyllium compounds that contain a Be(η^5-C_5H_5) fragment,[1] there are only a few in which the cyclopentadienyl ligand is substituted. The half-sandwich species, [(η^5-C_5Me_5)BeCl] (**1a**), was first isolated by Burns and Andersen in 1987,[2] and later by Pratten, Cooper, and Aroney, who also characterized the mixed-ring beryllocene [Be(C_5Me_5)(C_5H_5)] by solution IR and NMR studies.[3] From **1a**, the beryllium organometallic compunds [(η^5-C_5Me_5)BeMe],[4] [(η^5-C_5Me_5)Be(PtBu$_2$)],[5a] and [(η^5-C_5Me_5)Be(AstBu$_2$)][5b] were subsequently prepared. More recently the beryllocenes [Be(C_5Me_5)$_2$], [Be(C_5Me_4H)$_2$], and [Be(C_5Me_5)(C_5Me_4H)] have been described by some of us.[6]

Whereas [(η^5-C_5H_5)BeMe] has long been known,[7] the synthesis and physical properties of the C_5Me_5 analogue have not been published, despite its use in the formation of an [Yb]-Me[Be] adduct, by its reaction with the bent sandwich f block metallocene [Yb(η^5-C_5Me_5)$_2$].[4] Herein we report details on the formation of **2a** and the synthesis of other beryllium alkyls [η^5-C_5Me_5)BeR] as well as of [(η^5-C_5Me_5)BeCl] (**1a**; an alternative, higher-yield procedure[2]) and the bromo analogue **1b**. Compounds **1** are useful synthons for alkyl, cyclopentadienyl, and related Be(η^5-C_5Me_5) compounds, but attempts to make [(η^5-C_5Me_5)BeH], the simplest member of the series, starting from these or related derivatives, have failed to give a pure material.

As discussed in the preceding paper,[6] the beryllocenes [Be(C_5Me_5)$_2$], [Be(C_5Me_4H)$_2$], and [Be(C_5Me_5)(C_5Me_4H)] exhibit dynamic behavior in solution. To obtain chemical

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evidence in support of the proposed fluxional processes,[8] the reactions of the above beryllocenes with different Lewis bases have been examined. Some of these attempts have proved fruitless but nevertheless the reaction with CNXyl (Xyl = C_6H_3-2,6-Me_2) has provided convincing evidence of the existence, in solution, of different η^5/η^1 beryllocene isomers as active participants in the two fluxional processes. The synthesis, structural characterization (spectroscopic and X-ray methods) and solution behavior of the iminoacyl complexes [(η^5-Cp′)Be(C(NXyl)Cp″)] resulting from these reactions are also reported.[9]

Results and Discussion

Alkyl derivatives [(η^5-C_5Me_5)BeR] (R = Me, CMe_3, CH_2CMe_3, and CH_2Ph): Most of the compounds described in this section can be made from either [(η^5-C_5Me_5)BeCl][2, 3] (**1a**) or its bromo analogue [(η^5-C_5Me_5)BeBr] (**1b**), in Et_2O, or in mixtures of Et_2O and toluene, when heating is required. These halide precursors 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 [(η^5-C_5Me_5)BeR] (**2**), can then be obtained by metathetical exchange with an alkyl lithium reagent in Et_2O [Eq (1)].

$$\underset{\mathbf{1}}{[(\eta^5\text{-}C_5Me_5)BeX]} + LiR \longrightarrow \underset{\mathbf{2}}{[(\eta^5\text{-}C_5Me_5)BeR]} + LiX \qquad (1)$$

(X = Cl, **1a**; Br, **1b**) (R=Me, **2a**; CMe_3, **2b**; CH_2CMe_3, **2c**; CH_2Ph, **2d**)

Abstract in Spanish: *Los compuestos de composición [(η^5-C_5Me_5)BeX] (X = Cl, **1a**; Br, **1b**) se preparan con facilidad mediante la reacción de los haluros BeX_2 con M[C_5Me_5] (M = Na o K), y son excelentes materiales de partida para la síntesis de otros compuestos organometálicos de Be tales como los alquilos [(η^5-C_5Me_5)BeR] (R = Me, **2a**; CMe_3, **2b**; CH_2CMe_3, **2c**; CH_2Ph, **2d**). Estos últimos resultan de una simple reacción de metátesis entre **1a** o **1b** y el derivado LiR correspondiente. Los intentos efectuados para obtener el hidruro [(η^5-C_5Me_5)-BeH] han resultado infructuosos, debido casi con toda probabilidad a su tendencia a la desproporción para dar [Be(C_5Me_5)$_2$] y BeH_2. Si los berilocenos [Be(C_5Me_5)$_2$], [Be(C_5Me_4H)$_2$] y [Be(C_5Me_5)(C_5Me_4H)] se hacen reaccionar con el CNXyl se obtienen iminoacilos de formulación [(η^5-C_5Me_5)Be(C(NXyl)Cp′)] and [(η^5-C_5Me_4H)Be(C(Nxyl)Cp′)] (**3**–**6**), siendo Xyl = C_6H_3-2,6-Me_2 y Cp′ = C_5Me_5 or C_5Me_4H. El aislamiento de tres berilocenos diferentes de la reacción del [Be(C_5Me_5)(C_5Me_4H)] con CNXyl, a saber, los complejos **5a**, **5b** y **6** se puede considerar como evidencia concluyente sobre la existencia de diferentes berilocenos isómeros que se generan merced a dos procesos dinámicos de muy baja energía de activación:el desplazamiento sigmatrópico 1,5 de la unidad Be(η^5-Cp′) sobre la periferia del anillo η^1-Cp′ y el proceso de inversión molecular que intercambia la función de los dos anillos.*

Compounds **1** and **2** are crystalline solids, which may be crystallized on cooling their concentrated solutions in pentane. Their physical properties are given in the Experimental Section. The halides **1**, but not the alkyls **2**, develop a red coloration on standing in a glass vessel, that we attribute to the generation of hydrolysis products from the trace amounts of water on the glass surface. It is noteworthy that similarly to [(η^5-C_5H_5)BeCl] and other (η^5-C_5H_5)Be compounds,[10] **1a** experiences an observable benzene-induced ^1H NMR shift from $\delta = 1.91$ ppm in C_6D_{12} to $\delta = 1.67$ ppm in C_6D_6: $\delta =$ 0.24 ppm. This shift, albeit smaller than that of [Be(C_5H_5)Cl], ($\delta = 0.39$ ppm)[10] is larger than that spanned by the remaining Be(C_5Me_5) compounds described in this section, and may be attributed to specific interactions between the aromatic solvent and the H atoms of the Cp′ ligand,[10] which have a net positive charge in the dipolar molecules. The smaller average $\delta +$ charge on a C–H group of C_5Me_5, as compared with C_5H_5, and the fact that a molecule of C_6H_6 cannot interact simultaneously with the three H atoms of a CH_3 group explain the lower upfield shift found for **1a**, in comparison with its C_5H_5 analogue.

Compounds **1** and **2** are all volatile and can be sublimed readily under dynamic vacuum. The least volatile are the halides **1** (ca. 60 °C, 0.05 mm), whereas the methyl derivative **2a** sublimes at 60 °C and atmospheric pressure, or at room temperature under a dynamic vacuum of approximately 0.1 mm. Thus, care must be exercised in isolating this alkyl or it will distill into the solvent trap. All compounds give monomeric molecular ions in their mass spectra (see Experimental Section) and no ions are detected at masses greater than expected for monomeric fragments. In addition, no disproportionation ions (for example the molecular ion for [Be(C_5Me_5)$_2$]$^+$) have been observed.

NMR data for compounds **1** and **2** (^1H, ^{13}C, and ^9Be) compare well with those reported for other Cp′-Be derivatives. There is not much worthy of note in the ^1H NMR spectra, except the solvent dependence for **1a** already mentioned. The ^{13}C chemical shift of the Me group of [(η^5-C_5Me_5)BeMe] (**2a**) is $\delta = -25.4$ ppm and the signal appears as a well-resolved 1:1:1:1 pattern due to coupling to ^9Be ($I = 3/2$), with a ^1J(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 $\delta = 108$–109 ppm (see Experimental Section) is almost the same as that found for structurally characterized (η^5-C_5Me_5)Be compounds,[4] including the [(η^5-C_5Me_5)Be(C(NXyl)Cp′)] derivatives described in the following section (ca. $\delta = 10$ ppm). Hence, η^5-C_5Me_5 coordination to beryllium in compounds **1** and **2** can be proposed with confidence. ^9Be chemical shifts also have normal values. The signals are relatively sharp (half-height width of 3.5 Hz for **1b**; 16 Hz for **2a**) and due to paramagnetic ring current effects[11] they are located in the higher-field region of the ^{9}Be chemical shift range (from approximately $\delta = -25$ to $+25$ ppm[11–14]). They cluster around $\delta = -16$ ppm and are therefore somewhat shifted to lower field in comparison with values reported for [(η^5-C_5H_5)BeX] complexes ($\delta = -19.1$ ppm, X = Cl; $\delta = -20.4$ ppm, X = Me; δ – 21.9 ppm, X = C_5H_5[11, 12]).

The reactions of the alkyl derivatives are rather disappointing, since they are inert except to protic substances such as water. For example, the methyl compound **2a** is recovered unchanged after exposure to H_2 (18 atm, 20 °C) and it does not react with either $CNCMe_3$ or CNXyl (in the latter case at 80 °C for 24 h). This contrasts with the facility with which CNXyl adds to [$BeCp'_2$] complexes (vide infra). Similarly, the neopentyl derivative **2c** is also recovered unchanged when exposed to H_2 (18 atm), CO (18 atm), NO (2 atm), or N_2O (2 atm), at 20 °C. Even treatment of the benzyl derivative **2d** with H_2 (60 atm) at 110 °C for a week does not yield the hydride or its decomposition product, [Be(C_5Me_5)$_2$] (see below). Heating the *tert*-butyl complex **2b** in toluene for prolonged periods of time gave no evidence for the hydride. Thus, neither hydrogenation nor β-H transfer reactions are useful synthetic routes to the sought hydride [(η^5-C_5Me_5)BeH]. The lack of reactivity of compounds **2** is not, however, surprising, as in their molecules the four beryllium atomic orbitals are involved in the bonding to the η^5-C_5Me_5 and R groups. Hence, only high-energy antibonding orbitals could be employed so that any resulting ring-slipping or ion-pair formation would be a high energy processes.

The isolobal relationship between the alkyls **2** and the hydride [(η^5-C_5Me_5)BeH] suggests that the latter is a reasonable synthetic target. However, compounds with Be–H bonds are rare,[1b, 15] the only monomeric hydride structurally characterized by X-ray methods is [κ^3-HB(3-*t*Bupz)$_3$BeH] reported by Parkin and co-workers.[14a] Other terminal beryllium hydrides are known[16] such as the thermally unstable, partially characterized [(η^5-C_5H_5)BeH], which is reported to form when [(η^5-C_5H_5)Be(BH_4)] reacts with PPh_3.[1b] Since, as outlined above, the hydrogenolysis of the alkyls **2** fails to give the hydride, the reactions of the halides **1** with different hydride-transfer reagents have been investigated.

[(η^5-C_5Me_5)BeCl] reacts with $LiBH_4$ to give [(η^5-C_5Me_5)Be(BH_4)], but since the latter complex is recovered unchanged when treated with PPh_3, it was characterized only by IR spectroscopy. The analogous reaction of **1b** with $LiAlH_4$ in Et_2O appeared more promising since it provides a white crystalline solid that shows an IR absorption at 1950–1985 cm^{-1}, which may be due to a Be–H group.[1b] The frequency and relative intensity of this feature depends upon the reaction conditions, particularly the reaction time. However, no hydride resonance can be found by ^{1}H NMR spectroscopy, the spectrum exhibits only two singlets at $\delta = 1.66$ and 1.83 ppm. The former is due to unreacted **1b** and the latter to [Be(C_5Me_5)$_2$], as confirmed by comparison with the spectrum of an authentic sample.[17] ^{9}Be NMR studies also confirm the existence of [Be(C_5Me_5)$_2$] and [Be(C_5Me_5)Br] as the only species detectable in solution. As a further confirmation of the above, the mass spectrum of the white crystalline solid shows a molecular ion envelope at 223/225 amu, identical to that of pure **1b**, along with a higher mass envelope at 279 amu, due to [Be(C_5Me_5)$_2$]. In this regard it is also noteworthy that the reaction of [(η^5-C_5Me_5)BeCl] with $KC_{10}H_8$ also gives [Be(C_5Me_5)$_2$].

Control experiments were done to show that [(η^5-C_5Me_5)BeBr] (**1b**) is stable toward disproportionation. No evidence for the formation of [Be(C_5Me_5)$_2$] is found by ^{1}H NMR spectroscopy and mass spectrometry when **1b** is stirred in solution or sublimed. The same applies to the alkyls **2**, so that evidence for the formation of the metallocene is obtained only when **1b** is allowed to react with $LiAlH_4$. We suggest that [(η^5-C_5Me_5)BeH] forms, but it is not stable at room temperature and disproportionates as shown in Equation (2).

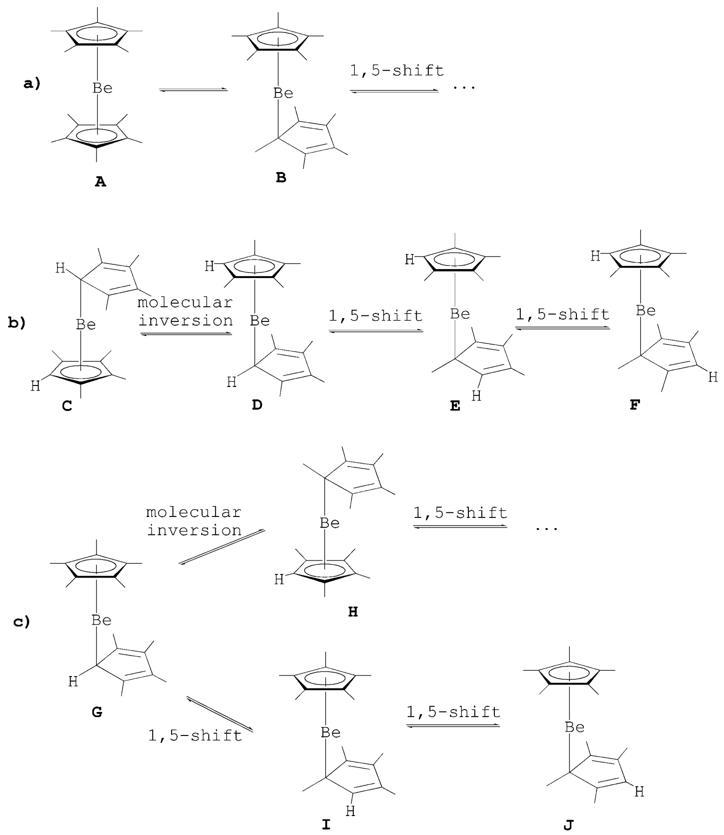
$$2\,[(\eta^5\text{-}C_5Me_5)BeH] \longrightarrow [Be(C_5Me_5)_2] + BeH_2 \qquad (2)$$

The reaction should be essentially thermoneutral, since an equal number of Be–H and Be–C_5Me_5 bonds are made and broken. Although we have been unable to confirm the formation of the unstable BeH_2,[18] it seems reasonable that its insolubility in hydrocarbon solvents, due to its polymeric nature, drives the disproportionation reaction.

In this regard it is appropriate to comment that similarly to other organometallic compounds of Be and other Group 2 and Group 12 elements,[19, 20] **1a** participates in a redistribution reaction when treated with pyridine, yielding insoluble [$BeCl_2$(py)$_2$], and [Be(C_5Me_5)$_2$]. Thus, it appears that the insolubility of one of the disproportionation products is the driving force for it.

Half-sandwich [(η^5-C_5Me_5)Be(C(NXyl)Cp′)] and related iminoacyls: solution studies: Beryllocene, [Be(C_5H_5)$_2$],[21] has a slip-sandwich η^5/η^1 (π) structure in the solid state.[22] In solution it is a highly fluxional molecule that undergoes two facile rearrangements, namely a 1,5-sigmatropic shift of the Be(η^5-C_5H_5) unit around the periphery of the η^1 ring and a molecular inversion that interchanges the roles of the C_5H_5 rings.[8]

At variance with this situation, [Be(C_5Me_5)$_2$] has an η^5/η^5, almost regular sandwich structure in the solid state. As discussed in the preceding paper,[6] variable-temperature ^{1}H and ^{13}C NMR studies provide no evidence for dynamic behavior. However, by similarity with other beryllocenes it is reasonable to assume that in solution the η^5/η^5 structure (**A** in Scheme 1 a) is in equilibrium with the η^5/η^1 structure (**B**). Rearrangement by means of 1,5-sigmatropic shifts and ring-exchange would convert **B** into degenerate structures. [Be(C_5Me_4H)$_2$] exhibits a slip-sandwich structure in the solid state (degenerate formulae **C** or **D**, Scheme 1 b), but in solution the two rings are equivalent, even at −90 °C. This is indicative of ring-exchange between degenerate structures **C** and **D**, but whereas it is reasonable to suppose that the 1,5-shift is a very easy process, no evidence can be obtained by NMR spectroscopy, even if this exchange would lead to the nondegenerate, isomeric structures **E** and **F**. Finally, in the solid state [Be(C_5Me_5)(C_5Me_4H)] contains η^5-C_5Me_5 and η^1-C_5Me_4H, the latter bonded to Be through the CH carbon atom. For this beryllocene, variable-temperature NMR studies denote flux-

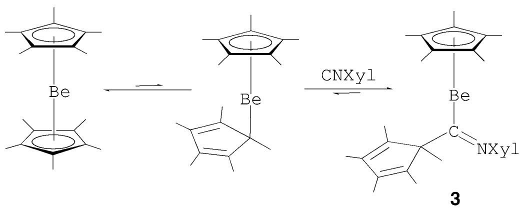


Scheme 1. Rearrangements of substituted beryllocenes: a) $[Be(C_5Me_5)_2]$; b) $[Be(C_5Me_4H)_2]$; c) $[Be(C_5Me_5)(C_5Me_4H)]$.

ionality,[6] but provide no clues about its intimate nature. As shown in Scheme 1c, both the molecular inversion and the sigmatropic shift generate isomeric structures (**H** and **I**, **J**, respectively).

To obtain evidence in support of the structures and processes represented in Scheme 1 we have investigated the reactions of substituted beryllocenes, $[BeCp'_2]$,[6] toward some Lewis bases. Dissapointingly, no coordination or ion-pair formation is detected by NMR spectroscopy when $[Be(C_5Me_5)_2]$ is heated (80 °C, 16 h) in C_5D_5N. Moreover, decamethylberyllocene is recovered unchanged after treatment with CO (20 °C, 2 atm) or 1,3,4,5-tetramethylimidazol-2-ylidene (100 °C). $[Be(C_5Me_4H)_2]$ is also recovered unaltered after exposure to 100 atm of CO. Notwithstanding the above, we have found that octa-, nona-, and decamethylberyllocene exhibit a remarkable reactivity toward CNXyl that serves as a chemical probe for both the sigmatropic shift and the molecular inversion rearrangements.

The room-temperature reaction of $[Be(C_5Me_5)_2]$ and CNXyl allows isolation in good yields (ca. 70%) of a crystalline solid, identified as the iminoacyl complex **3** (Scheme 2). Relevant spectroscopic data in support of this formulation include an IR absorption at 1570 cm^{-1} associated with a low-field ^{13}C resonance at $\delta = 155.7$ ppm, which are due to the iminoacyl unit,[24] along with ^{13}C signals characteristic of the η^5 ring ($\delta = 108.8$ ppm) and of the C_5Me_5 group within the iminoacyl ligand ($\delta = 140.7$, 135.2, and 71.7 ppm).



3

Scheme 2. Reaction of $[Be(C_5Me_5)_2]$ and CNXyl.

Other spectroscopic features of **3** are in agreement with the proposed structure (see Experimental Section), subsequently confirmed by X-ray studies (vide infra).

It is worthy of note that iminoacyl formation is a reversible reaction. Room-temperature ^1H and ^{13}C NMR studies of **3** provide no indication of reversibility, but at higher temperatures partial dissociation of the product into the reactants is observed. At temperatures between approximately 80 and 115 °C, the equilibrium is attained at a convenient rate and the equilibrium concentration of the species involved can be measured. This leads to the van't Hoff representation shown in Figure 1 and to ΔH^o and ΔS^o values of 18(0.4) kcal mol^{-1} and 35(1) cal mol^{-1}K^{-1}, respectively, for the dissociation reaction. Extrapolation to room temperature yields an equilibrium constant of 2×10^{-6} for the formation of **3**. Iminoacyl formation is thermodynamically favored at 20 °C, despite the negative ΔS^o value. Clearly, this is due to the enthalpic contribution, but at temperatures around 100 °C the $T\delta S^o$ term offsets partially the exothermicity of the iminoacyl forming reaction,[23–25] and leads to partial dissociation measurable by NMR methods. As illustrated in Scheme 2 and discussed in more detail below, the carbon–carbon coupling reaction involves, most likely, the η^5/η^1 isomer of $[Be(C_5Me_5)_2]$, structure **B** of Scheme 1a. Compelling evidence in favor of this proposal derives from studies of other beryllocenes (vide infra) and of the isovalent zincocene $[Zn(C_5Me_5)_2]$. The latter has a slip-sandwich structure[26a,b] and reacts with CNXyl to give the iminoacyl $[(\eta^5\text{-}C_5Me_5)Zn(C(NXyl)C_5Me_5)]$, with properties very similar to those of **3**.[26c]

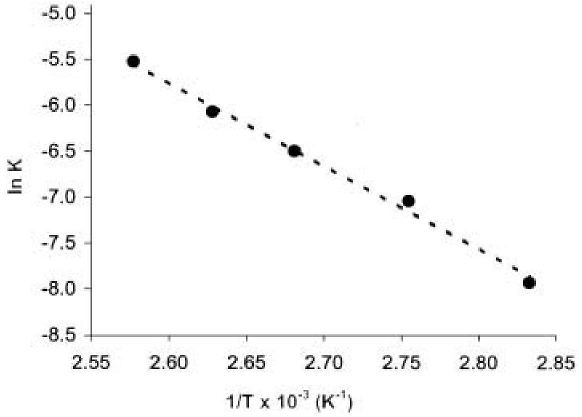
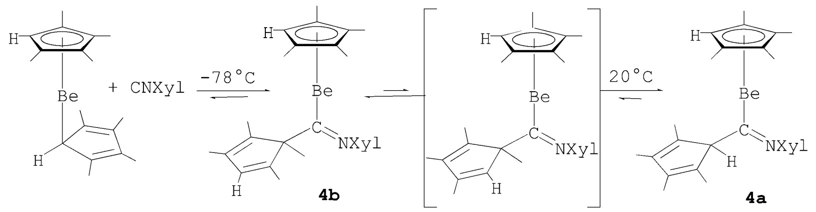


Figure 1. Van't Hoff representation for the dissociation process of complex **3**.

The analogous room-temperature reaction of $[Be(C_5Me_4H)_2]$ and CNXyl gives the iminoacyl derivative **4a** (Scheme 3), with a structure similar to that of **3**. Apart from a ν(CN) value of 1560 cm^{-1}. ^1H NMR resonances are found for **4a** at $\delta = 4.69$ (η^5-Cp′) and 3.96 ppm (−C(NXyl)Cp′) for the C*H* proton of the Cp′ groups. The ring carbon atoms of the η^5-C_5Me_4H ligand resonate at $\delta = 100.4$ (*C*H), 110.2, and 111.5 ppm (tentatively assigned to the β and α carbon atoms, respectively), whereas those of the other Cp′ ring appear at distinctively higher ($\delta = 77.2$ ppm; *C*H) and lower field ($\delta = 137.3$ and 134.6, α and β carbon nuclei). It seems clear that **4a** results from the coupling of CNXyl with beryllocene **C** (or **D**) of Scheme 1b. However, if the reaction is conducted at −78 °C, a different isomer, **4b**, is generated cleanly and may be isolated in almost 55 % yield. Salient NMR features of **4b** are an olefinic ^1H resonance at $\delta = 5.78$ ppm, due to the C_5Me_4H proton of the iminoacyl ligand, as well as five distinct ^{13}C signals for the ring carbon nuclei of this C_5Me_4H group ($\delta = 71.8$ ppm aliphatic quaternary carbon; $\delta = 134.1$, 141.3, and 148.6 ppm, olefinic quaternary carbons; $\delta = 131.4$ ppm, olefinic *C*H). These data indicate that **4b** is the product of the reaction of beryllocene **F** (Scheme 1b) and CNXyl, or in other words that one of the β-C(Me) atoms of the η^1 ring of $[Be(C_5Me_4H)_2]$ couples with the isocyanide to produce **4b**.

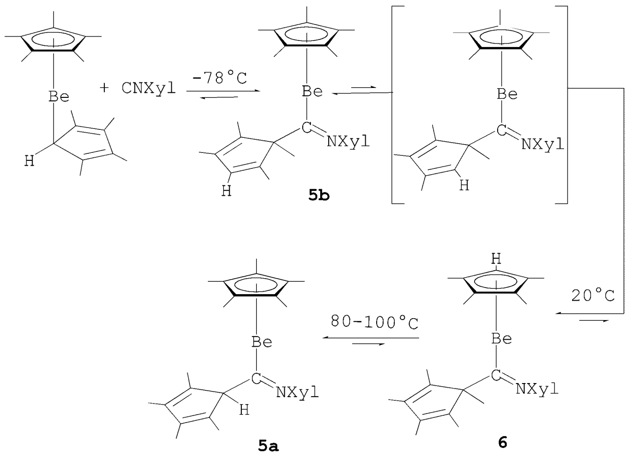


Scheme 3. Reaction of $[Be(C_5Me_4H)_2]$ with CNXyl.

Even though compound **4b** is stable at room temperature in the solid state, in solution it undergoes partial dissociation even at −78 °C (^1H NMR monitoring). Warming a C_7D_8 solution of **4b** prepared at −78 °C, allows the observation at approximately −30 °C of a weak olefinic ^1H resonance at $\delta = 5.69$ ppm. This may be due to the missing iminoacyl isomer, namely the one in brackets in Scheme 3, that would result from the α-C(Me)-CNXyl coupling of beryllocene **E** in Scheme 1b. Nevertheless the concentration of this purported iminoacyl remains too low (< 5 %) to allow its unequivocal characterization. At room temperature, **4b** converts cleanly into **4a**, hence the latter is the thermodynamic product of the reaction. Isolation of the two products provide direct experimental evidence for the existence of the η^5/η^1 isomers **C** and **F** of Scheme 1b, and therefore for the 1,5-sigmatropic rearrangement responsible for their exchange. Naturally, the identity of the two Cp′ rings makes molecular inversion undetectable by this chemical probe. As discussed in the next paragraphs, nonamethylberyllocene allows this problem to be circumvented.

Four isomeric structures (Scheme 1c) are possible for $[Be(C_5Me_5)(C_5Me_4H)]$, thus it is not surprising that its reaction with CNXyl is the most complex of all that we have examined. Three of the four possible iminoacyl isomers (Scheme 4) have been isolated and characterized, and of the three, **5a**, **5b**, and **6**, the last two have been studied by X-ray methods. As for $[Be(C_5Me_4H)_2]$, the low-temperature reaction of $[Be(C_5Me_5)(C_5Me_4H)]$ and CNXyl yields the iminoacyl resulting from β-C(Me)-CNXyl coupling of the C_5Me_4H group (**5b**).

An isolated sample of this complex, dissolved at −78 °C, exists in equilibrium with minor amounts of the reactants. Upon warming to room temperature, slow conversion to the isomeric iminoacyl **6** takes place, but once more, at approximately −30– −20 °C, a weak ^1H NMR resonance at $\delta = 5.69$ ppm can be discerned. The concentration of this species remains below 5 % too, and therefore it cannot be confidently attributed to the missing imnoacyl isomer, represented in brackets in Scheme 4. Further prolonged heating at 80–100 °C, causes the formation of a new compound, **5a**, at the expense of the lower temperature isomers **5b** and **6**.

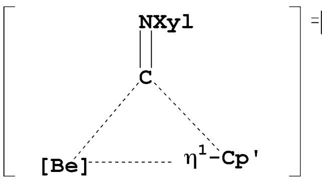


Scheme 4. Reaction of $[Be(C_5Me_5)(C_5Me_4H)]$ with CNXyl.

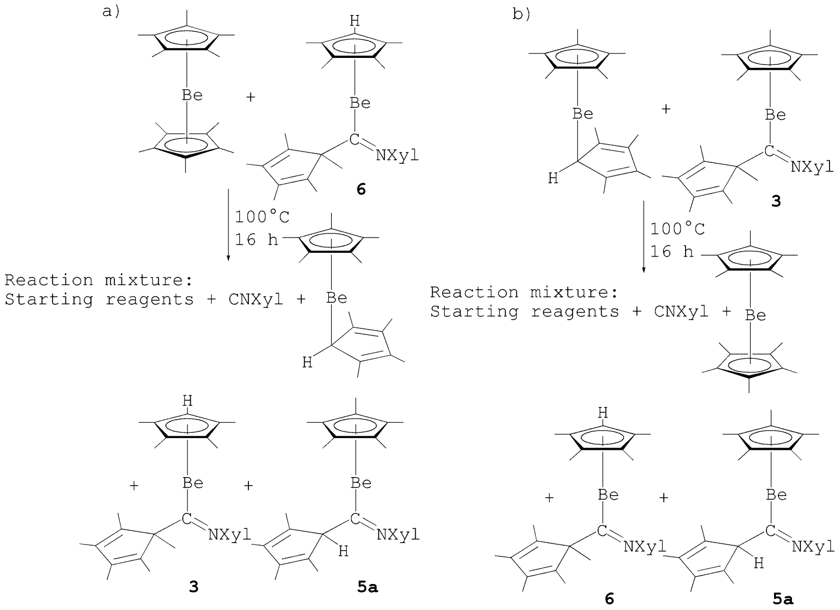
Spectroscopic data show unambiguously that **6** contains an η^5-C_5Me_4H ligand, whereas the C_5Me_5 of the original beryllocene is part of the iminoacyl unit (see Experimental Section). Thus, it is the product of the coupling of CNXyl with the *inverted* beryllocene **H** of Scheme 1c. This result provides convincing evidence for the population of structure **H**, and therefore for the molecular inversion process that exchanges the two rings of the beryllocenes. On a preparative scale, **6** can be obtained by the direct room temperature reaction of $[Be(C_5Me_5)(C_5Me_4H)]$ and CNXyl. As already hinted, **6** is not the thermodynamic product of this reaction, since at higher temperatures (80–100 °C) it converts readily into **5a**, which has an η^5-C_5Me_5 ligand and an iminoacyl with a C(NXyl)−CHC_4Me_4 bond. Obviously, **5a** derives from isomer **G** of Scheme 1c.

All of the above results concerning the iminoacyls **3**–**6** can only be accounted for assuming that the C–C coupling that leads to the iminoacyl unit is a reversible reaction. This has been convincingly demonstrated for **3** (see Figure 1), and it is additionally supported by the results of the crossing experiments represented in Scheme 5. In one instance (Scheme 5a), equimolar amounts of [Be(C_5Me_5)$_2$] and of iminoacyl **6** are heated in C_7D_8, at 100 °C for 16 h, to give a complex reaction mixture that contains [Be(C_5Me_5)$_2$], **6**, CNXyl, **3**, and **5a**. In the second experiment (Scheme 5b), the iminoacyl **3** and the mixed-ring beryllocene [Be(C_5Me_5)(C_5Me_4H)] are reacted under identical conditions, to generate a mixture of the starting products plus CNXyl, [Be(C_5Me_5)$_2$] and the iminoacyls **6** and **5a**. These results may be interpreted postulating that in each case the iminoacyl reactant undergoes partial dissociation and that the liberated CNXyl combines with the beryllocenes present in solution to furnish the corresponding iminoacyls.

The reaction of the Me-substituted beryllocenes with CNXyl to form the iminoacyls **3**–**6** resembles the analogous addition of organolithium and organomagnesium reagents to isonitriles to give the corresponding metalloimines,[27, 28] which are useful synthetic reagents.[24a] Ion-pair formation, followed by coordination of the isocyanide and rearrangement to the final product, seems unlikely considering the chemical reactivity described above for the beryllocenes, and also in view of the facility with which iminoacyls **4b** and **5b** form at −78 °C in pentane. A concerted [4+2] cycloaddition between the diene part of the η^1-Cp′ ring and the isocyanide π system cannot be ruled out but, in our view, it is difficult to reconcile with the sequence of formation found experimentally for the iminoacyl products of Scheme 3 and Scheme 4. We believe that our experimental results are best explained assuming that a three-center transition state of type **K** gives rise to the iminoacyl products. This could arise from the direct attack of CNXyl onto a weak, inherently polar, Be–η^1-Cp′ bond (recall that [(η^5-C_5Me_5)BeMe], with a stronger bond between Be and the primary alkyl, does not react with CNXyl at 80 °C), or, alternatively, from a traditional migratory insertion process.[23, 24a] The latter appears unlikely as the investigated beryllocenes are sterically congested molecules and moreover the metal has only 2s and 2p valence orbitals available. However, since a change in the hapticity of the η^5-Cp′ ligand cannot be discarded, we defer making a definitive proposal on this matter until the results of the theoretical studies that are currently under way become available.



K



Scheme 5. Crossing experiments showing the reversibility of the iminoacyl forming reactions.

The [Be(C_5Me_5)(C_5Me_4H)]/CNXyl reaction system may be used to illustrate our mechanistic proposal, which rests on the assumption that all accessible [Be(η^5-Cp′)(η^1-Cp″)] isomers compete to react with the isocyanide. At a certain reaction temperature, the nature of the iminoacyl product (e.g. **5a**, **5b**, or **6** in Scheme 4) depends on both the relative rate of the individual couplings and the relative thermodynamic stability of the iminoacyl isomers. Recalling that the difference in energy between the ground state structure **G** and the highest energy isomer **H** (Scheme 1c) is only[6] approximately 4 kcal mol^{-1}, the selective, fast generation of **5b** at −78 °C (Scheme 4) implies that **J** is populated at this temperature and moreover that its reaction with CNXyl is fastest, perhaps as a reflection of a very weak Be–C bond.[29] The reversibility of the reaction and the higher thermodynamic stability of **6**, as compared to **5b**, accounts for the **5b**-to-**6** conversion observed at 20 °C. Nevertheless, this reaction is slower, and requires higher temperatures and longer reaction times. Finally, the most stable isomer **5a** forms only after prolonged heating at 80–100 °C. This may be due to a higher kinetic barrier for the coupling reaction, as a consequence of the stronger Be–CH bond[29] within the Be–η^1-C_5Me_4H linkage of the ground state structure **G**.

Solid-state structure of iminoacyls [(η^5-Cp′)Be(C(NXyl)Cp″)]: Although characterization of the half-sandwich beryllium iminoacyls by spectroscopy is unambiguous, it was considered important to attain further characterization by X-ray methods. Three derivatives have been chosen for this investigation, two of them, namely **3** and **5b**, contain a Be(η^5-C_5Me_5) unit, the third, **6**, is a Be(η^5-C_5Me_4H) derivative that results from the reaction of CNXyl with the inverted beryllocene structure **H** of Scheme 1c. Compound **5b** arises from beryllocene isomer **J** (Scheme 1c) and therefore results from βC(Me)−CNXyl bond coupling.

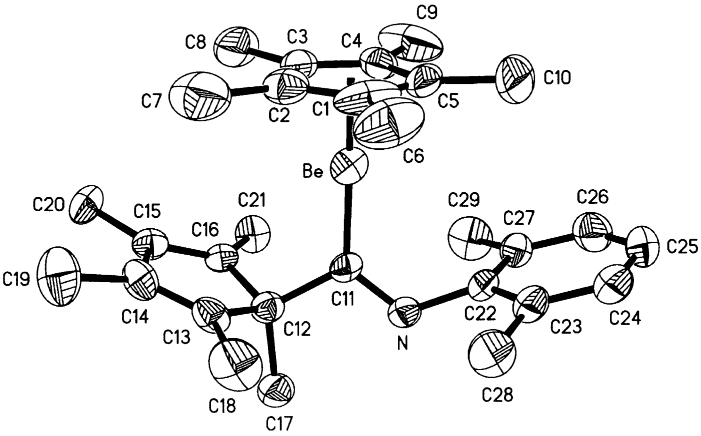


Figure 2. Structure of complex **3** (ORTEP diagram).

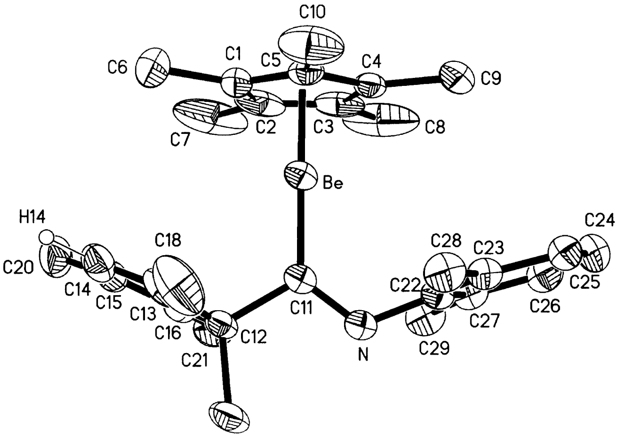


Figure 3. Structure of complex **5b** (ORTEP diagram).

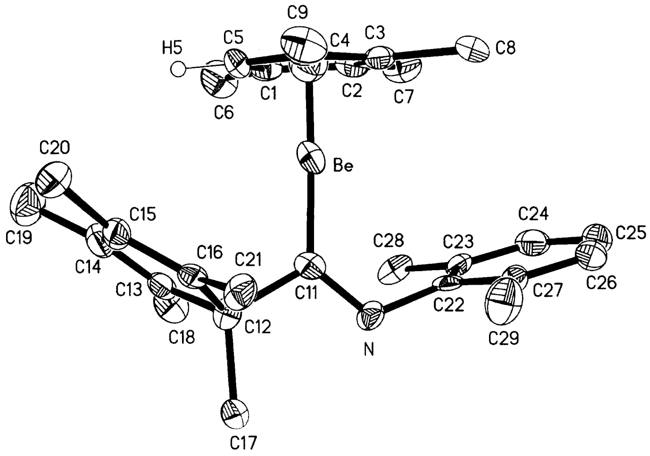


Figure 4. Structure of complex **6** (ORTEP diagram).

Table 1. Crystal data and structure refinement.

	3	**5b**	**6**
formula	$C_{29}H_{39}BeN$	$C_{28}H_{37}BeN$	$C_{28}H_{37}BeN$
formula weight	410.62	396.60	396.60
crystal size [mm]	0.20 × 0.20 × 0.25	0.15 × 0.32 × 0.40	0.08 × 0.18 × 0.20
crystal system	triclinic	monoclinic	monoclinic
space group	$P\bar{1}$	$P2_1/n$	$P2_1/n$
a [Å]	8.6728(7)	15.5994(9)	10.678(2)
b [Å]	16.751(2)	18.8313(10)	19.128(3)
c [Å]	18.357(2)	16.9993(9)	12.273(2)
α [°]	99.5050 (10)	90	90
β [°]	103.4820 (10)	102.6930(10)	105.825 (4)
γ [°]	90.4370 (10)	90	90
V [Å^3]	2554.8(4)	4871.6(5)	2411.6(7)
Z	4	8	4
ρ_{calcd} [Mg m^{-3}]	1068	1081	864
T [K]	143(2)	153(2)	143(2)
μ [mm^{-1}] (Mo$_{K\alpha}$)	0.060	0.061	0.061
F(000)	896	1728	864
θ_{max} [°]	20.81	32.06	20.82
index ranges	$-8 \leq h \leq 8$ $-16 \leq k \leq 14$ $-16 \leq l \leq 18$	$-6 \leq h \leq 22$ $-28 \leq k \leq 25$ $-17 \leq l \leq 22$	$-2 \leq h \leq 10$ $-16 \leq k \leq 17$ $-12 \leq l \leq 10$
no. of reflections measd	7641	20791	4870
no. of unique reflections	5049	10881	2197
no. of params	566	571	286
R_1 ($I > 2\sigma(I)$)[a]	0.1000	0.0818	0.0690
R_1 (all data)	0.1331	0.1418	0.1432
wR_2 (all data)	0.3029	0.2469	0.1742
diff. Fourier peaks min/max [e Å^{-3}]	−0.650/0.962	−0.387/0.532	−0.209/0.208

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

Figures 2, 3, and 4 show ORTEP perspective views of the molecules of the iminoacyls; crystal data collection parameters are summarized in Table 1. Table 2 provides a comparison of relevant bonding parameters. The Be-η^5-C_5Me_5 moiety of **3** and **5b** is characterized by a Be−Cp′(centroid) separation of 1.47 Å and Be−C$_{(ring)}$ lengths of 1.90 Å. These distances are identical, within the error of the measurement, to corresponding distances in the mixed-ring beryllocene [Be(η^5-C_5Me_5)(η^1-C_5Me_4H)],[6] revealing comparable bonding interactions. Interestingly, in compound **6**, which contains a Be(η^5-C_5Me_4H) linkage, the Be−Cp′(centroid) is longer (1.50 Å), consequently the Be−C$_{(ring)}$ are also longer (av 1.92 Å) and span a somewhat larger range than in **3** and **5b** (0.02 Å for the former and approximately 0.03 for **6**). It seems that to compensate for the slightly weaker Be−η^5-Cp′ interaction, the Be−C11 bond (to the iminoacyl carbon) is stronger in **6** than in **3** or **5b** (Table 2). Notwithstanding these small differences, in the three compounds the Be−C bond length is comparable to the Be−η^1-CH separations in the beryllocenes [Be($C_5Me_4H)_2$] and [Be(C_5Me_5)(C_5Me_4H)],[6] and it is within the 1.70–1.85 Å range characteristic of Be−C σ bonds. The η^5-Cp′(centroid)-Be-C11 angle is very close to 180°.

As for the iminoacyl ligand, the iminoacyl carbon atom C11 has a planar, triangular geometry, the sum of the three angles defined by this atom being 360°. In the three compounds the Be-C11-N angle opens up somewhat (ca. 127°), at the expense of the N-C11-C12 angle (ca. 113°) perhaps to minimize van

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

	3	**5b**	**6**
Be–C(η^5-ring)(av)	1.899(11)	1.900(4)	1.923(10)
Be–Cp′(ring centroid)	1.472(4)	1.470(4)	1.50(1)
Be–C11	1.752(11)	1.751 (4)	1.717(10)
centroid-Be-C11	178.7(5)	178.2(2)	176.8(5)
C11=N	1.282(7)	1.287(3)	1.287(6)
Be-C11-N	126.7(6)	126.4(2)	126.9(5)

der Waals repulsive interactions between the η^5-Cp′ and Xyl aromatic rings. The C11–N bond has a length of 1.29 Å, comparable to organic C=N bonds (1.26–1.31 Å[30]) and to the C=N bond of other main group iminoacyls.[31]

It is pertinent to comment that the Cp′ rings bonded to the iminoacyl carbon atom have localized, diene character. Brief structural comparison with the η^1-C_5Me_4H ring of [Be($C_5Me_4H)_2$] and [Be(C_5Me_5)(C_5Me_4H)] is therefore appropriate. As in these beryllocenes, the η^1-ring keeps partial aromatic character. For instance, the Be-bound carbon atom has nearly trigonal prismatic coordination, with Be-C-C angles close to 100°.[6] Additionally, in the beryllocenes the difference in the length of the $C_{\beta\beta}$ and $C_{\alpha\beta}$ bonds is of only 0.06–0.07 Å.[6] These data contrast with corresponding parameters in the iminoacyls, as the geometry around C12 is tetrahedral and the difference between the long ($C_{\beta\beta}$) and the short ($C_{\alpha\beta}$) carbon-carbon bonds is of the order of 0.14 Å.

Conclusions

The halides [(η^5-C_5Me_5)BeX] **1** have proved to be excellent starting materials for the preparation of other (η^5-C_5Me_5)Be organometallic compounds, including the alkyls [(η^5-C_5Me_5)BeR] **2**, and the beryllocenes [Be($C_5Me_5)_2$] and [Be(C_5Me_5)(C_5Me_4H)] described in the preceding paper.[6] The reactions of these two metallocenes and that of the analogous [Be($C_5Me_4H)_2$] with CNXyl give iminoacyl complexes of composition [(η^5-Cp′)Be(C(NXyl)Cp″)] **3**–**6**, where Cp′ and Cp″ stand for C_5Me_5 or C_5Me_4H. On the assumption that iminacyls **3**–**6** result from the coupling of [(η^5-Cp′)Be(η^1-Cp′)] isomers with the organic isocyanide, the isolation of iminoacyls **5a** and **5b** from the reaction of [Be(C_5Me_5)(C_5Me_4H)] and CNXyl (Scheme 4) provides chemical evidence for 1,5-sigmatropic shifts of the (η^5-C_5Me_5)Be unit around the periphery of the η^1-C_5Me_4H ring, whereas the formation of iminoacyl **6** (Scheme 4) attests to the feasibility of the molecular inversion rearrangement that exchanges the [Be(η^5-C_5Me_5)(η^1-C_5Me_4H)] and [Be(η^5-C_5Me_4H)(η^1-C_5Me_5)] isomers of this beryllocene. To the best of our knowledge these results constitute the first chemical demonstration provided for these dynamic rearrangements of metallocenes.

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 an oxygen-free argon atmosphere with conventional Schlenk techniques. Solvents were rigorously dried over sodium and degassed before use. The petroleum ether had a b.p. of 40–60°C. The complexes [Be($C_5Me_5)_2$], [Be($C_5Me_4H)_2$], and [Be(C_5Me_5)(C_5Me_4H)] were prepared according to literature procedures.[6] Microanalyses were obtained at the Microanalytical Services of the University of California, Berkeley and IIQ (Sevilla). Infrared spectra were recorded on a Bruker, Vector 22 spectrometer. NMR spectra were recorded on Bruker AMX-300, DRX-400 and DRX-500 or JEOL FX-90Q spectrometers. The ^{1}H and ^{13}C resonances of the solvent were used as the internal standard, and chemical shifts are reported relative to TMS. The mass spectra were obtained at the Mass spectroscopy facility at the University of California, Berkeley, and are reported as follows: molecular ion (observed intensity, simulated intensity).

Compound 1a, [(C_5Me_5)BeCl]: The diethyl ether adduct of $BeCl_2$, [$BeCl_2(OEt_2)_2$] (1.6 g, 0.012 mol) dissolved in diethyl ether (50 mL) was added to sodium pentamethylcyclopentadienide (2.0 g, 0.012 mol) in diethyl ether (50 mL). The mixture was stirred for 24 h and the volatile material was removed under reduced pressure. Pentane (50 mL) was added and the suspension was stirred for 10 min then allowed to settle. Filtration yielded a colorless filtrate that was concentrated to approximately 20 mL and cooled to −80°C to yield colorless blocks. The compound sublimed at 55–65°C at 10^{-2} mm. Yield 1.6 g, 75%; m.p. 109–110°C (turned red); ^{1}H NMR (90 MHz, [D$_6$]benzene, 25°C): $\delta = 1.67$ ppm (s, 15H; Cp′CH_3); ^{13}C NMR (22.5 MHz, [D$_6$]benzene, 25°C): $\delta = 8.40$ (s; CH_3), 109.3 ppm (s; CCH_3); ^{1}H NMR (90 MHz, [D$_{12}$]cyclohexane, 25°C): $\delta = 1.91$ (s, 15H; Cp′CH_3, turned reddish); MS (EI): *m/z*: 179 (100, 100), 180 (11, 29), 181 (33, 31), 182 (4, 3); elemental analysis calcd (%) for $C_{10}H_{15}BeCl$: C 66.9, H 8.4; found: C 67.0, H 8.3.

The compound may be obtained from K[C_5Me_5] with similar yield or from [Mg($C_5Me_5)_2$], but in the latter case the yield is about 20% when diethyl ether was used as solvent. The yield increased to 55% when the solvent mixture of toluene/diethyl ether (1:1) under reflux was used.

Compound 1b, [(C_5Me_5)BeBr]: This compound was prepared in a manner similar to that used for the chloride, except that [$BeBr_2(OEt_2)_2$] was used. The bromide was crystallized in 40% yield from hot hexane by cooling to room temperature; m.p. 117–119°C. The compound sublimed at 70–80°C at 10^{-2} mm. ^{1}H NMR (90 MHz, [D$_6$]benzene, 25°C): $\delta = 1.66$ (s, 15H; Cp′CH_3); ^{9}Be NMR ([D$_6$]benzene, 25°C): $\delta = -15.2$ ($w_{1/2} = 3.5$ Hz); MS (EI): *m/z*: 223 (100, 100), 224 (11, 61), 225 (98, 93), 226 (11, 5); elemental analysis calcd (%) for $C_{10}H_{15}BeBr$: C 53.6, H 6.7; found: C 53.1, H 6.6.

Compound 2a, [(C_5Me_5)BeMe]: Methyllithium (6.2 mL of a 0.90 M solution in diethyl ether, 0.0056 mol) was added to [(C_5Me_5)BeCl] in diethyl ether (50 mL), and the suspension was stirred for 8 h. The diethyl ether was evaporated and the residue was sublimed on to a cold finger (−78°C) at 30–40°C. The sublimed solid may be crystallized from a minimum volume of pentane at −10°C as colorless blocks. M.p. 64–65°C; ^{1}H NMR (90 MHz, [D$_6$]benzene, 25°C): $\delta = 1.77$ (s, 15H; Cp′CH_3), −1.25 ppm (s, 3H; Me); ^{13}C NMR (22.5 MHz, [D$_6$]benzene, 25°C): $\delta = 9.05$(s; CCH_3), 108.2 (s; CCH_3), −25.4 ppm ($J_{Be,C} = 29$ Hz; Be–CH_3); ^{9}Be NMR ([D$_6$]benzene, 25°C): $\delta = -16.7$ ppm ($w_{1/2} = 16$ Hz); ^{13}C NMR (22.5 MHz, [D$_6$]benzene, 80°C): $\delta = 8.92$(s; CCH_3), 108.4 (s; CCH_3), −26.1 ppm ($J_{Be,C} = 30$ Hz; Be–CH_3); MS (EI): *m/z*: 159 (100, 100), 160 (12, 12); elemental analysis calcd (%) for $C_{11}H_{18}Be$: C 83.0, H 11.3; found: C 83.1, H 11.0. Note: The methyl derivative is much more volatile than the halide derivatives and care must be taken when solvent is removed or it will be lost; accordingly the yield is variable.

Compound 2b–d, [(C_5Me_5)BeR]: These alkyls were prepared in a manner similar to **2a**. The three compounds, R = CMe_3, **2b**; CH_2CMe_3, **2c**; CH_2Ph, **2d**; are rather volatile and they were all collected by sublimation on to a cold finger at temperatures of about 40°C (CMe_3 and CH_2CMe_3) and 50°C (CH_2Ph). In each case the colorless solids may be crystallized from a minimum volume of pentane at low temperature (−30°C). In each case, the yields are variable, but generally are about 50%. **2b**: M.p. 72–74°C; ^{1}H NMR (90 MHz, [D$_6$]benzene, 25°C): $\delta = 1.72$ (s, 15H; Cp′CH_3), 0.92 ppm (s, 9H; CMe_3); ^{13}C NMR (22.5 MHz, [D$_6$]benzene, 25°C): $\delta = 8.53$ (s; CCH_3), 108.2 (s; CCH_3), 32.1 ppm (s; CMe_3); MS (EI): *m/z*: 201 (100, 100), 202 (14, 16), 203 (1,1); elemental analysis calcd (%) for $C_{14}H_{24}Be$: C 83.6, H 11.9; found: C 82.9, H 12.0.

2c: M.p. 20 °C; ^{1}H NMR (90 MHz, [D$_6$]benzene, 25 °C): $\delta = 1.76$ (s, 15H; Cp′CH$_3$), 1.0 (s, 9H; CH$_2$C*Me*$_3$), −0.35 ppm (s, 2H; C*H*$_2$CM$_3$); MS (EI): *m*/*z*: 215 (100, 100), 216 (6, 17); elemental analysis calcd (%) for C$_{15}$H$_{26}$Be: C 83.7, H 12.1; found: C 83.1, H 12.0.

2d: M.p. 57–59 °C; ^{1}H NMR (90 MHz, [D$_6$]benzene, 25 °C): $\delta = 1.62$ (s, 15H; Cp′CH$_3$), 1.15 (s, 2H; C*H*$_2$CMe$_3$), 6.9 (m, 4H; CH$_p$+CH$_o$ − Ph), 7.1 (m, 2H; CH$_m$–Ph); MS (EI): *m*/*z*: 237 (100, 100), 238 (18, 20); elemental analysis calcd (%) for C$_{17}$H$_{22}$Be: C 86.3, H 9.4; found: C 86.0, H 9.3.

Compound 3: Decamethylberyllocene [Be(C$_5$Me$_5$)$_2$], (0.279 g, 1 mmol) and 2,6-dimethylphenylisocyanide, CNXyl (Xyl = C$_6$H$_3$-2,6-Me$_2$) (0.131 g, 1 mmol), were dissolved in petroleum ether (30 mL) and stirred overnight at room temperature. Removal of the solvent in vacuo, extraction with petroleum ether and filtration afforded crystals of **1** after cooling the filtrate at −30 °C. Yield: 0.3 g, 73 %; ^{1}H NMR (500 MHz, [D$_6$]benzene, 25 °C): $\delta = 1.40$ (s, 3H; C(NXyl)C$_5$*Me*$_5$), 1.44 (s, 15H; η^5-C$_5$*Me*$_5$), 1.73 (s, 6H; C(NXyl)C$_5$*Me*$_5$), 1.83 ppm (s, 6H; C(NXyl)C$_5$*Me*$_5$); ^{13}C NMR (125 MHz, [D$_6$]benzene, 25 °C): $\delta = 8.7$ (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 ppm (s; *C*=N); IR (Nujol): $\tilde{\nu} = 1571$ cm^{-1} (C=N); elemental analysis calcd (%) for C$_{29}$H$_{39}$NBe (410.6): C 84.9, H 9.5, N 3.4; found: C 84.8, H 9.6, N 3.4.

Compound 4a: The synthesis is similar to that of compound **3**. From octamethylberyllocene, [Be(C$_5$Me$_4$H)$_2$], (0.251 g, 1 mmol) and CNXyl (0.131 g, 1 mmol), approximately 0.26 g (68 %) of crystalline **2a** were obtained. ^{1}H NMR (400 MHz, [D$_6$]benzene, 25 °C): $\delta = 1.36$ (s, 6H; η^5-C$_5$*Me*$_4$H), 1.55 (s, 6H; η^5-C$_5$*Me*$_4$H), 1.77 (s, 6H; C(NXyl)C$_5$*Me*$_4$H), 1.86 (s, 6H; C(NXyl)C$_5$*Me*$_4$H), 3.96 (s, 1H; C(NXyl)C$_5$Me$_4$*H*), 4.69 ppm (s, 1H; η^5-C$_5$Me$_4$*H*); ^{13}C NMR (125 MHz, [D$_6$]benzene, 25 °C): $\delta = 8.8$ (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 ppm (s; *C*=N); IR (Nujol): $\tilde{\nu} = 1560$ cm^{-1} (C=N); elemental analysis calcd (%) for C$_{27}$H$_{35}$NBe (382.6): C 84.8, H 9.2, N 3.7; found: C 85.0, H 9.2, N 3.7.

Compound 4b: [Be(C$_5$Me$_4$H)$_2$], (0.251 g, 1 mmol) and CNXyl (0.131 g, 1 mmol) were dissolved in petroleum ether (30 mL) at −78 °C and stirred at this temperature for 30 min. The reaction mixture was allowed to warm up to −20 °C and the solvent was then evaporated in vacuo at this temperature. The residue was extracted with petroleum ether, cooled to −20 °C, filtered and crystallized at that temperature. Yield: 0.21 g, 55 %; ^{1}H NMR (400 MHz, [D$_8$]toluene, −78 °C): $\delta = 1.24$ (s, 3H; η^5-C$_5$*Me*$_4$H), 1.25 (s, 3H; η^5-C$_5$*Me*$_4$H), 1.53 (s, 3H; η^5-C$_5$*Me*$_4$H), 1.55 (s, 3H; η^5-C$_5$*Me*$_4$H), 1.57 (s, 3H; C(NXyl)C$_5$*Me*$_4$H), 1.67 (s, 3H; C(NXyl)C$_5$*Me*$_4$H), 1.74 (s, 3H; C(NXyl)C$_5$*Me*$_4$H), 1.80 (s, 3H; C(NXyl)C$_5$*Me*$_4$H), 4.65 (s, 1H; η^5-C$_5$Me$_4$*H*), 5.78 ppm (s, 1H; C(NXyl)C$_5$Me$_4$*H*); ^{13}C NMR (125 MHz, [D$_8$]toluene, −78 °C): $\delta = 8.9$ (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 ppm (s; *C*=N); IR (Nujol): $\tilde{\nu} = 1560$ cm^{-1} (C=N); elemental analysis calcd (%) for C$_{27}$H$_{35}$NBe (382.6): C 84.8, H 9.2, N 3.7; found: C 84.7, H 9.8, N 3.7.

Compound 5a: [Be(C$_5$Me$_5$)(C$_5$Me$_4$H], (0.075 g, 0.283 mmol) and CNXyl (0.037 g, 0.283 mmol) were dissolved in toluene (20 mL). The mixture was stirred at 100 °C for 48 h in a thick-walled Schlenk tube. The solvent was removed in vacuo and the resulting residue was extracted with petroleum ether. After filtering the solution and concentrating the filtrate, the clear solution was cooled at −30 °C overnight and crystals were collected. Yield: 0.05g, 45 %; ^{1}H NMR (500 MHz, [D$_6$]benzene, 25 °C): $\delta = 1.44$ (s, 15H; η^5-C$_5$*Me*$_5$), 1.78 (s, 6H; C$_5$*Me*$_4$H), 1.87 (s, 6H; C$_5$*Me*$_4$H), 2.15 (s, 6H; C(NXyl)), 4.01 (s, 1H; C$_5$Me$_4$*H*), 6.89 (t, ^3J(H,H) = 7 Hz, 1H; *p*-C*H*-Ar), 7.07 (d, ^3J(H,H) = 7 Hz, 2H; *m*-C*H*-Ar); ^{13}C NMR (125 MHz, [D6$_8$]benzene, 25 °C): $\delta = 8.9$ (s; η^5-C$_5$*Me*$_5$), 11.7 (s; C$_5$*Me*$_4$H), 13.4 (s; C$_5$*Me*$_4$H), 19.8 (s; 2Me-Ar), 78.0 (s; *C*H-C$_5$Me$_4$H), 109.1 (s; η^5-*C*$_5$Me$_5$), 121.5 (s; *p*-*C*H-Ar), 125.4 (s; Cq-Ar), 128.0 (s; *m*-*C*H-Ar), 134.4 (s; *C*$_5$Me$_4$H), 137.0 (s; *C*$_5$Me$_4$H), 156.2 ppm (s; C=N); IR (Nujol): $\tilde{\nu} = 1570$ cm^{-1}(C=N); elemental analysis calcd (%) for C$_{29}$H$_{39}$NBe (396.6): C 84.9, H 9.3, N 3.5; found: C 84.0, H 9.5, N 3.6.

Compound 5b: The synthesis is similar to that of compound **4b**. Starting from [Be(C$_5$Me$_5$)(C$_5$Me$_4$H)], (0.265 g, 1 mmol) and CNXyl (0.131 g, 1 mmol), approximately 0.22 g (55 %) of **5b** were obtained by crystallization from petroleum ether. ^{1}H NMR (400 MHz, [D$_8$]toluene, −78 °C): $\delta = 1.44$ (s, 15H; η^5-C$_5$*Me*$_5$), 1.63 (s, 3H; C$_5$*Me*$_4$H), 1.74 (s, 3H; C$_5$*Me*$_4$H), 1.80 (s, 3H; C$_5$*Me*$_4$H), 1.89 (s, 3H; C$_5$*Me*$_4$H), 2.06 (s, 6H; C(NXyl)), 5.85 (s, 1H; C$_5$Me$_4$*H*), 7.00 (s, ^3J(H,H) = 7 Hz, 1H; *p*-C*H*-Ar), 7.08 ppm (d, ^3J(H,H) = 7 Hz, 2H; *m*-C*H*-Ar); ^{13}C NMR (125 MHz, [D$_8$]toluene, −78 °C): $\delta = 9.2$ (s; η^5-C$_5$*Me*$_5$), 11.4 (s; C$_5$*Me*$_4$H), 13.5 (s; C$_5$*Me*$_4$H), 14.2 (s; C$_5$*Me*$_4$H), 18.8 (s; C$_5$*Me*$_4$H), 20.0 (s; 2Me-Ar), 72.2 (s; *C*$_5$Me$_4$H), 108.9 (s; η^5-*C*$_5$Me$_5$), 121.1 (s; *p*-*C*H-Ar), 124.7 (s; Cq-Ar), 128.0 (s; *m*-*C*H-Ar), 131.1 (s; *C*H-C$_5$Me$_4$H), 133.6 (s; *C*$_5$Me$_4$H), 141.5 (s; *C*$_5$Me$_4$H), 148.3 (s; *C*$_5$Me$_4$H), 155.8 ppm (s; C=N); IR (Nujol): $\tilde{\nu} = 1570$ cm^{-1} (C=N); elemental analysis calcd (%) for C$_{29}$H$_{39}$NBe (396.6): C 84.9, H 9.3, N 3.5; found: C 84.1, H 9.8, N 3.5.

Compound 6: [Be(C$_5$Me$_5$)(C$_5$Me$_4$H)], (0.265 g, 1 mmol) and CNXyl (0.131 g, 1 mmol) were dissolved in petroleum ether (20 mL) and the mixture was stirred at room temperature for 16 h. Removal of the solvent in vacuo, extraction with petroleum ether and filtration afforded crystals of **3a** after cooling the concentrated filtrate at −30 °C. Yield: 0.19 g, 48 %; ^{1}H NMR (500 MHz, [D$_6$]benzene, 25 °C): $\delta = 1.33$ (s, 6H; η^5-C$_5$*Me*$_4$H), 1,45 (s, 3H; C$_5$*Me*$_5$), 1.59 (s, 6H; η^5-C$_5$*Me*$_4$H), 1.74 (s, 6H; C$_5$*Me*$_5$), 1.81 (s, 3H; C$_5$*Me*$_5$), 2.05 (s, 6H; CNXyl), 4.70 (s, 1H; η^5-C$_5$*Me*$_4$*H*), 6.89 (t, ^3J(H,H) = 7 Hz, 1H; *p*-C*H*-Ar), 7.04 ppm (d, ^3J(H,H) = 7 Hz, 2H; *m*-C*H*-Ar); ^{13}C NMR (125 MHz, [D$_6$]benzene, 25 °C): $\delta = 8.5$ (s; η^5-C$_5$*Me*$_4$H), 10.7 (s; η^5-C$_5$*Me*$_4$H), 11.0 (s; C$_5$*Me*$_5$), 11.5 (s; C$_5$*Me*$_5$), 16.6 (s; C$_5$*Me*$_5$), 19.5 (s; CNXyl), 71.2 (s; *C*$_5$Me$_5$), 100.6 (s; η^5-*C*$_5$Me$_4$H), 109.6 (s; η^5-*C*$_5$Me$_4$H), 111.2 (s; η^5-*C*$_5$Me$_4$H), 120.9 (s; CNXyl), 125.2 (s; CNXyl), 128.0 (s; CNXyl), 135.6 (s; *C*$_5$Me$_5$), 140.5 (s; *C*$_5$Me$_5$), 156.4 ppm (*C*=N); IR (Nujol) $\tilde{\nu} = 1570$ cm^{-1} (C=N); elemental analysis calcd (%) for C$_{29}$H$_{39}$NBe (396.6): C: 84.9, H: 9.3, N: 3.5, found C: 84.5, H: 9.4, N: 3.5.

Crystal structure determinations: The crystals of **3**, **5b** and **6** used for X-ray studies were obtained by crystallization from petroleum ether. Experimental procedures were as in the preceding paper.[6] Crystal data and experimental details are given in Table 4.

CCDC-151965 (**3**), CCDC-203559 (**5b**) and CCDC-203558 (**6**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge at www.ccdc.cam.ac.uk/conts/retrieving.html or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or e-mail: deposit@ccdc.cam.ac.uk

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