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The synthesis and characterisation of two novel cyclopentadienylberyllium compounds

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Abstract

The syntheses of pentamethylcyclopentadienylberyllium chloride ($CpMe_5BeCl$) and the previously unreported pentamethylcyclopentadienylcyclopentadienylberyllium ($CpMe_5BeCp$) are described. The NMR and IR spectra of the two compounds are reported and discussed in terms of the bonding of the latter compound. The reaction between pentamethylcyclopentadienylberyllium chloride and dicyclopentadienylberyllium ($BeCp_2$) is also described.

Introduction

The work described below represents an extension of our previous work [1,2] on the controversy surrounding the structure and bonding of dicyclopentadienylberyllium (beryllocene). Pentamethylcyclopentadienylberyllium chloride ($CpMe_5BeCl$) was prepared as the result of attempts to synthesise the decamethyl derivative of dicyclopentadienylberyllium. It was then found that when solutions of $CpMe_5BeCl$ and $BeCp_2$ were mixed, $CpMe_5BeCp$ and CpBeCl were formed. Since we believed that the mixed ring compound $CpMe_5BeCp$ might provide valuable insight into the $BeCp_2$ story, considerable effort was expended to obtain a pure sample for further study. The results of this effort are presented below.

Experimental

All solvents used in this work were meticulously dried and de-oxygenated immediately before use. Reactions were carried out by Schlenk techniques, and solutions were transferred by syringe and cannula via rubber septa. The extremely

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air-sensitive cyclopentadienylberyllium compounds were most conveniently transferred by vacuum sublimation; this had the added advantage that some purification takes place during each transfer. Melting points were determined on samples sealed in glass tubes under vacuum.

Beryllium chloride was unpacked in a nitrogen-filled glove-box, sieved to remove any beryllium oxide, and then transferred into Schlenk solid-addition tubes. Pentamethylcyclopentadiene was prepared by the method of Threlkel and Bercaw [3] from 2-bromo-2-butene, distilled under reduced pressure, then dried over sodium wire. CpBeCl was prepared as described earlier [1].

Infrared spectra were recorded from 4000 to 250 cm^{-1} on a Perkin Elmer 457G double beam grating spectrophotometer using a 0.2 mm pathlength CsI solution cell fitted with rubber septa. Various solvents were used to overcome the problem of solvent absorption. The spectra were calibrated with polystyrene film and are believed to be accurate to ± 4 cm^{-1} above 2000 cm^{-1} and ± 2 cm^{-1} below 2000 cm^{-1}. A Bruker WM-400 instrument was used for the recording of NMR spectra. The solutions, containing TMS as an internal reference, were sealed under nitrogen in 5 mm tubes. The mass spectrum of $CpMe_5BeCl$ was recorded on an A.E.I. MS12 single focusing instrument by directly connecting a tube containing the sample to the gas inlet port. The inlet and source temperatures were 40 and 150 °C respectively, and an ionising voltage of 70 eV was used.

Synthesis of $CpMe_5BeCl$

Butyllithium (1.6 *M* in n-hexane, 57 ml) was added to pentamethylcyclopentadiene (12.8 g) at -78 °C and the mixture stirred as it was allowed to warm slowly to room temperature. The resulting white precipitate of lithiumpentamethylcyclopentadienide was filtered off and then washed with n-pentane (3×20 ml). Diethyl ether (100 ml) was added, and the mixture cooled to -78 °C. To the slurry, a solution of beryllium chloride (3 g) in diethyl ether (200 ml) was added slowly (10 min) with stirring. After a further 3 h stirring at room temperature the solvent was removed under reduced pressure and the product, contaminated with pentamethylcyclopentadiene, was sublimed (0.1 mmHg) into another flask. This crude product was then dissolved in a minimum of n-hexane and the solution cooled to 0 °C. After 48 h the supernatant liquor was removed via a cannula through a rubber septum, leaving large colourless crystals. These were resublimed to yield crystals (1.4 g, 25% yield) of m.p. 110–112 °C. The product was found to react violently with water and to decompose rapidly in air via highly coloured purple intermediates *.

A sample of the product was decomposed in distilled water and the chlorine content determined by titration with silver nitrate. Although the end-point was difficult to discern, the chlorine content was close to that expected for $CpMe_5BeCl$ (found 17.7 ± 2%; calc. 19.7%).

The identity of this compound was also confirmed by mass spectrometry. The fragmentation observed included the cleavage of the beryllium to ring bond, as well as successive loss of methyl substituents from the parent molecule. Fragmentation involving the loss of chlorine from the beryllium–ring moiety only occurred after the loss of three or more of the methyl groups.

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* The synthesis of $CpMe_5BeCl$ was first reported by S.J. Pratten in 1985 [4]; more recently it was prepared by the reaction of bis(pentamethylcyclopentadienyl)magnesium with beryllium chloride [5].

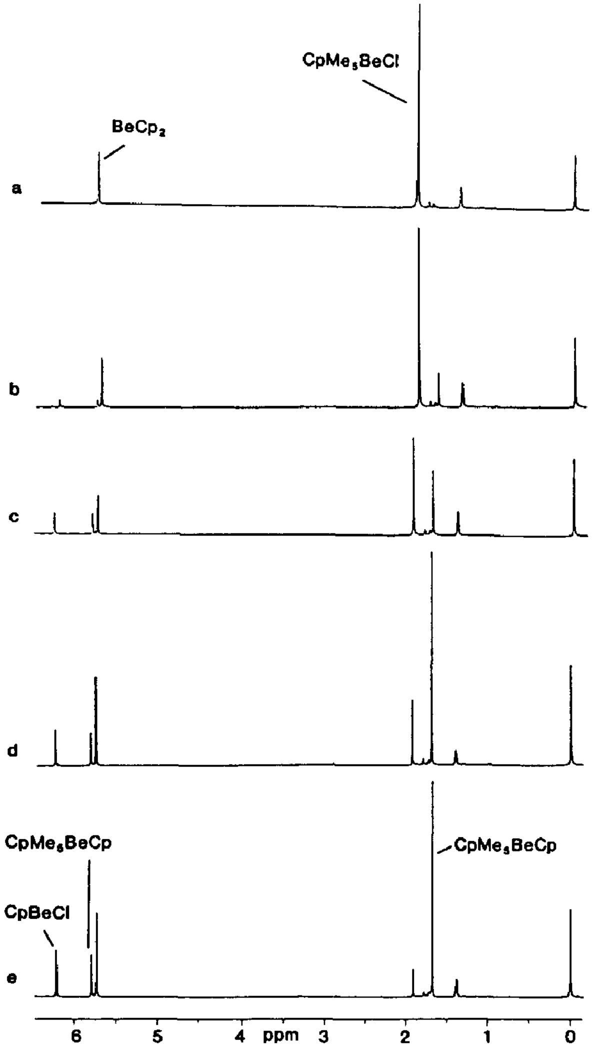

Fig. 1. 400 MHz ^{1}H NMR spectra of $BeCp_2$ added to $CpMe_5BeCl$ in C_6D_{12} after (a) 2 min, (b) 1 h, (c) 3 h, (d) 8 h, and (e) 1 week.

Reaction between $CpMe_5BeCl$ *and* $BeCp_2$

Solutions of $CpMe_5BeCl$ and $BeCp_2$ (in C_6D_{12} or $CDCl_3$) were mixed and the resulting reaction monitored by ^{1}H NMR spectroscopy. The peaks due to $BeCp_2$ and $CpMe_5BeCl$ were seen to diminish in intensity with time as three new peaks appeared (Fig. 1). This can be explained in terms of the equilibrium;

$$BeCp_2 + CpMe_5BeCl \rightleftharpoons CpMe_5BeCp + CpBeCl$$

Equilibrium was reached faster in $CDCl_3$ than in C_6D_{12}, and was found to lie further to the right in the polar solvent.

Synthesis of $CpMe_5BeCp$

Attempts to prepare a pure sample of the mixed ring compound by the reaction of CpBeCl and $LiCpMe_5$ in a solvent were hampered by the equilibrium between the desired product and the CpBeCl reactant, as discussed above. In order to

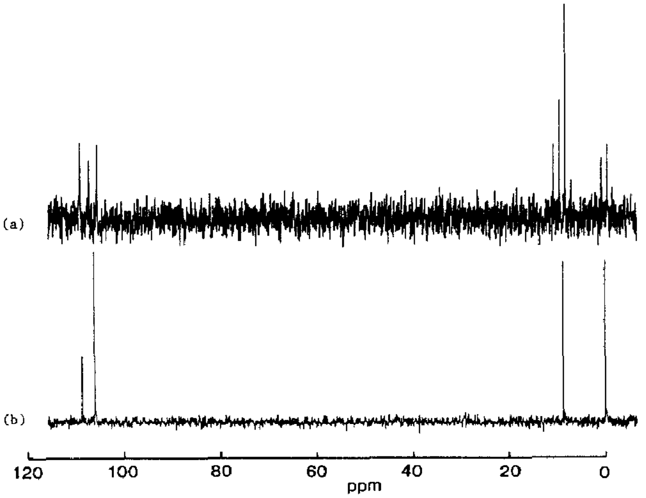

Fig. 2. 400 MHz ^{13}C NMR spectra of $CpMe_5BeCp$ recorded at 25 °C in C_6D_6; (a) fully coupled, and (b) proton decoupled.

Table 1

^{13}C NMR data for cyclopentadienyl beryllium compounds at 25 °C [a]

Compound	Solvent	Ring carbons			Methyl carbons	
		δ	^1J (C–H)	^2J (C–H)	δ	^1J (C–H)
$BeCp_2$	C_6D_{12}	107.5	168	6		
$CpMe_5BeCl$	C_6D_{12}	109.6		[b]	8.83	127
$CpMe_5BeCp'$	C_6D_6	108.6		[b]	8.67	125
		106.0'	161	6		

[a] Chemical shifts are given as δ values in ppm downfield from TMS and coupling constants are in Hz.
[b] Coupling was not resolved.

overcome this problem, the reaction was performed in the absence of a solvent: CpBeCl (2.9 g) was melted (60 °C) in the presence of a stoichiometric excess of $LiCpMe_5$, prepared as above, and the mixture was kept at 60 °C for 4 h in a 50 ml Schlenk flask then extracted with n-pentane (5 × 20 ml). The combined extracts were reduced in volume to give a good yield of a yellow wax-like product. This was found by ^1H NMR spectroscopy to contain mostly $CpMe_5BeCp$, but with some contamination by $CpMe_5BeCl$, which was then removed by careful fractional sublimation *. After repeated slow sublimations, colourless, air-sensitive crystals of m.p. 25–27 °C were obtained that gave a ^1H NMR spectrum consisting of two sharp peaks. Additional evidence for the characterisation of the compound was obtained from the fully coupled and proton decoupled ^{13}C NMR spectra (Fig. 2 and Table 1). The ^1H–^{13}C coupling pattern observed is as expected for $CpMe_5BeCp$.

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* $CpMe_5BeCp$ was the least volatile beryllium compound encountered in this study.

Results and discussion

Infrared spectra

The basis of this study is that π-bonded, σ-bonded, and ionically-bonded cyclopentadienyl groups exhibit characteristic vibrational spectra [6,7]. Comparison of the IR spectra of $BeCp_2$, CpBeCl, and CpBeBr with those of $FeCp_2$, CpHgCl, and $HgCp_2$, led to the conclusion that in $BeCp_2$ one ring is bonded in a pentahapto and the other in a monohapto fashion [1]. In this work, the IR spectrum of $CpMe_5BeCp$ has been compared with those of $CpMe_5BeCl$, $Fe(CpMe_5)_2$, and

Table 2

Comparison of IR data (cm^{-1}) for $Fe(CpMe_5)_2$, $CpMe_5BeCl$, $CpMe_5BeCp$, and $BeCp_2$

$Fe(CpMe_5)_2$ [a]	$CpMe_5BeCl$ [b]	$CpMe_5BeCp$ [c]	$BeCp_2$ [d]
		3910w, b	3910w
			3170vw
			3110sh
		3075s	3080s
			3050sh
2980s			
2960s	2960m	2975s	
2910vs	2930vs	2927s	
2865s	2875s	2865s	
	2780vw	2780vw	
		2765vw	
2715w	2740w	2735m	
		1750vw, b	
1478m	1495w	1495w	
1452m	1450vs, b	1445s, b	
1428m			1410sh
1378s	1384s	1380s	
		1365sh	1365m
		1105w, sh	1106w
1075mw		1065w, sh	
	1055vs		
1032ms		1040m	
	1010m	990m	
			915sh
	905vvs		
			890sh
		835s, b	829m
		795w	
		775m	770ms
		735vs	
		660m	663s
595w		595m	
515mw			
455s			
375m	390s		
		368m	
		338s	

[a] From Ref. 8. [b] Recorded in CCl_4. [c] Recorded in C_6D_6 and CS_2. [d] Peaks due to the monohapto ring only (from Ref. 1).

$BeCp_2$ in an attempt to elucidate the nature of the bonding in the mixed-ring compound. The spectral data are shown in Table 2. In the case of $BeCp_2$, only the peaks that were previously assigned to the vibrations of the monohapto Cp-ring are listed [1]. The compound $CpMe_5BeCl$ could reasonably be expected to have C_{5v} symmetry with a pentahapto ring as for CpBeCl *. Evidence for this comes from a comparison of the IR spectrum of $CpMe_5BeCl$ with that of $Fe(\eta^5\text{-}CpMe_5)_2$. Similarities are apparent, though the spectra are, of course, not identical.

The spectrum of $CpMe_5BeCl$ can be expected to exhibit two intense absorptions due to the beryllium–ring and beryllium–chlorine stretching vibrations, as found previously for $BeCp_2$, CpBeCl, and CpBeBr [1]; however, assignment of the beryllium–ligand frequencies was beyond the scope of this work.

The spectrum of $CpMe_5BeCp$ shows virtually all of the spectral characteristics for a pentahapto $CpMe_5$ group, as observed for both $Fe(CpMe_5)_2$ and $CpMe_5BeCl$. This strongly suggests that $CpMe_5BeCp$ in solution has a pentahapto-bonded $CpMe_5$ ring.

It can reasonably be inferred that the Cp group in $CpMe_5BeCp$ is not pentahapto, since the two very distinct peaks found for CpBeCl, CpBeBr and $BeCp_2$ at ca. 1015 and 1125 cm^{-1}, and the combinations and overtones between 1800 and 2700 cm^{-1} due to the pentahapto Cp-ring [1] are absent from the spectrum of $CpMe_5BeCp$. On the other hand, the strongest peak assigned [1] to a vibration of the monohapto Cp group in $BeCp_2$ (at 663 cm^{-1}) is clearly present, albeit at relatively lower intensity, at 660 cm^{-1} in the spectrum of $CpMe_5BeCp$. Similarly, peaks at 775, 1105, and 1365 cm^{-1} in the spectrum of $CpMe_5BeCp$ match closely peaks assigned [1] to the vibrations of the monohapto bonded Cp-ring in $BeCp_2$. It has been argued [10] that the peaks at 965 and 740 cm^{-1} in the spectrum of $BeCp_2$ are also indicative of a monohapto Cp ring and not beryllium–ligand vibrations as assigned in ref. 1; these may correspond to the peaks at 990 and 735 cm^{-1} in $CpMe_5BeCp$. Taken together, these observations indicate that the compound referred to above as $CpMe_5BeCp$ is in fact $(\eta^5\text{-}CpMe_5)Be(\eta^1\text{-}Cp)$.

NMR spectra

The ^1H NMR chemical shifts determined for the two compounds in C_6D_{12} and C_6D_6 are compared with those for CpBeCl, CpBeBr, and $BeCp_2$ in Table 3. Whereas upfield aromatic solvent-induced shifts (ASIS) are observed for the Cp protons of CpBeCl and CpBeBr [2], the Cp group of $CpMe_5BeCp$ exhibits a downfield shift in the aromatic solvent, reflecting the electron donating power of the $CpMe_5$ substituent.

The 400 MHz ^1H NMR spectrum recorded at 25°C for $CpMe_5BeCp$ consists of two sharp peaks with integrals in the expected ratio of 3/1. In view of the conclusion from the IR spectra, the appearance of only two peaks indicates fluxional behaviour of the monohapto Cp-ring. Low-temperature ^1H NMR spectra were recorded for this compound (400 MHz) in a mixture of CCl_2F_2 and toluene-d_8 in an attempt to "freeze out" this dynamic behaviour. The peak widths at half-height were measured and normalised with respect to the width of the peak due to the

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* X-ray crystallographic analysis of a single crystal of $CpMe_5BeCl$ was attempted [9]. The study indicated that the compound was of C_{5v} symmetry, but, the degree of refinement was insufficient for publication of the structure.

Table 3

^{1}H NMR shifts for cyclopentadienyl beryllium compounds at 25 °C [a]

Solute	Solvent	
	C_6D_{12}	C_6D_6
CpBeCl	6.27	5.66
CpBeBr	6.30	5.66
$BeCp_2$	5.73	5.68
$CpMe_5BeCl$	1.91	1.69
$CpMe_5BeCp$	5.79	6.01
	1.68	1.51

[a] Chemical shifts are given as δ values in ppm downfield from TMS.

Table 4

^{1}H NMR peak widths (Hz) at half-height for $CpMe_5BeCp$ at various temperatures (400 MHz)

Temperature (°C)	observed		normalized	
	Cp	$CpMe_5$	Cp	$CpMe_5$
−50	3.8	6.7	3.8	6.7
−100	4.6	6.7	4.6	6.7
−135	6.7	7.0	6.4_5	6.7
−138	5.8	6.1	6.5	6.7

$CpMe_5$ group, and the results are listed in Table 4. The observed broadening of the peak due to the Cp protons relative to that of the methyl peak suggests a slowing down of the "ring whizzing" at the lower temperatures. This is consistent with the conclusion drawn above from the IR spectra. It is possible, though, that this slight broadening may be due to viscosity effects in the solvent near its freezing point of ca. −140 °C.

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