

The formation and structure of pentamethylcyclopentadienylmercuric chloride

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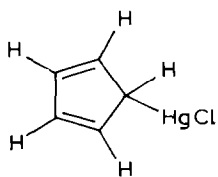
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Abstract

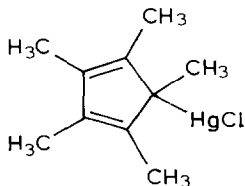
Pentamethylcyclopentadienylmercuric chloride has been prepared in 70% yield from a reaction between pentamethylcyclopentadienyllithium and mercuric chloride in THF solution. NMR studies on C_5Me_5HgCl have demonstrated that the C_5 -ring is obviously σ -bonded to the metal, but undergoes intramolecular rearrangements via 1,2-shifts, as previously observed for C_5H_5HgCl . Earlier reports of the synthesis and NMR spectral behavior of bis(pentamethylcyclopentadienyl)mercury are questioned.

Introduction

The synthesis and structures of cyclopentadienylmercury compounds have attracted considerable interest and controversy since the initial report of dicyclopentadienylmercury, $(C_5H_5)_2Hg$, in 1956 [1]. In 1969, one of us described the results of variable temperature 1H NMR studies that clearly showed the related mercurial C_5H_5HgCl (**1**) to be a fluxional species with a nuclear configuration of



(1)



(2)

lowest free energy in which the C_5H_5 moiety is η^1 -bonded to the mercury atom [2]. A similar conclusion was independently reached by others, on the basis of ^{13}C NMR spectroscopy of **1** [3] and studies of related indenylmercury compounds [4,5].

Although comparisons of pentamethylcyclopentadienyl- and cyclopentadienyl-metal systems are now commonplace in organometallic chemistry, such comparisons have been much less extensively made in organomercury chemistry. Bis(pentamethylcyclopentadienyl)mercury, $(C_5Me_5)_2Hg$, was first reported in 1969 and was assigned a "static" η^1 -bonded structure [6], although the formulation of this product as an organomercury compound now appears to be in error (vide infra). Herein we describe the synthesis of the related compound pentamethylcyclopentadienylmercuric chloride, $(C_5Me_5)HgCl$ (**2**), and the results of variable temperature 1H , ^{13}C and ^{199}Hg investigations which demonstrate that **2** has a limiting η^1 -bonded structure analogous to **1**.

Results and discussion

Bis(pentamethylcyclopentadienyl)mercury was reportedly synthesized by a reaction of lithium pentamethylcyclopentadienide with $HgCl_2$ in THF solution [6]. The product was described as colorless crystals, m.p. 125–126 °C. A room temperature 1H NMR spectrum of the product in benzene solution exhibited 3 singlets with areas in the ratio 2/2/1. On the basis of these data, the product was identified as $(C_5Me_5)_2Hg$ in which the cyclopentadienyl substituents were η^1 -bonded to the mercury atom.

Unfortunately, no experimental details of the synthesis or elemental analyses of the product were given. All attempts in our laboratory to repeat this synthesis have been unsuccessful. The 1H NMR spectra of the products did exhibit the 3 proton resonances described, and were always identical with the 1H NMR spectrum of decamethyl-1,1'-dihydrofulvalene, prepared earlier by us [7] and also by Jutzi and Kohl [8]. We therefore agree with the conclusion reached by the latter authors that the product obtained by Illuminati and coworkers [6] was in fact the dimeric hydrocarbon decamethyl-1,1'-dihydrofulvalene, and not bis(pentamethylcyclopentadienyl)mercury as originally postulated.

In view of these results, we decided to undertake a synthesis and NMR spectral investigation of pentamethylcyclopentadienylmercuric chloride, **2**. Compound **2** was readily prepared from a reaction between equimolar amounts of lithium pentamethylcyclopentadienide and $HgCl_2$ in THF solution at $-78^\circ C$, followed by warming of the reaction mixture to room temperature. The product was obtained in ca. 70% yield after recrystallization from pentane. It did not exhibit a definite melting point, but slowly decomposed on heating.

Temperature dependent 1H , ^{13}C and ^{199}Hg NMR spectra

1H NMR. The 1H NMR spectrum of **2** (Tab. 1) exhibits only one signal with ^{199}Hg -satellites at room temperature. Upon cooling this signal broadens, and below coalescence temperature it splits into three signals in the ratio 2/2/1 (Fig. 1). We interpret these results in terms of a fluxional process involving metal carbon bond changes of a η^1 -bonded C_5Me_5 ligand via 1,2-shifts. The chemical shifts for the magnetically different methyl substituents can be assigned on the basis of the signal intensities and the magnitude of the ^{199}Hg - 1H -couplings. The energy barrier for the

Table 1

 ^1H , ^{13}C and ^{199}Hg NMR Spectra ^a of **2** at different temperatures

Temperature (°C)	^1H NMR ^b	^{13}C NMR ^c		^{199}Hg NMR ^d
	$\delta(\text{C}_5\text{Me}_5)$ [$J(\text{Hg}, \text{H})$ (Hz)]	$\delta(\text{C}_5\text{Me}_5)$ [$^1J(\text{Hg}, \text{C})$ (Hz)]	$\delta(\text{C}_5\text{Me}_5)$	$\delta(\text{Hg})$
+27	1.81 [85.7]	n.o.	13.4	-1350
-80	1.83(2), 1.75(2) 1.41(1)	133.9, 133.3 79.8 [1266]	17.7, 12.1, 11.1	-1350

^a In CD_2Cl_2 solution. ^b Chemical shifts (ppm) rel. to $\delta(\text{CH}_2\text{Cl}_2)$ 5.32. ^c Chemical shifts (ppm) $\delta(\text{CD}_2\text{Cl}_2)$ 53.8. ^d Chemical shifts (ppm) rel. to $\delta(\text{HgMe}_2)$ 0. n.o. = not observed.

sigmatropic rearrangement ΔG^\ddagger 46 kJ mol^{-1} (in toluene- d_8) is considerably higher than that for **1** (32.2 kJ mol^{-1} [3]) or $(\eta^1\text{-C}_5\text{H}_4\text{Me})_2\text{Hg}$ [9] but slightly lower than for the bis(indenyl) derivative $(\eta^1\text{-C}_9\text{H}_7)_2\text{Hg}$ (ΔG^\ddagger 54.0 kJ mol^{-1}) [10]. It is obvious that steric parameters determine the magnitude of the energy barrier for the rearrangement processes.

^{13}C NMR. The ^1H decoupled temperature dependent ^{13}C NMR spectra of **2** lead to conclusions similar to those reached from ^1H NMR spectra (Tab. 1). At room temperature only one signal can be detected for the five methyl substituents. The signal for the five ring carbon atoms is not visible, possibly owing to signal broadening that arises from rapid bonding exchange. The spectrum at -80°C , however, shows all the carbon atoms expected for a η^1 -bonded C_5Me_5 ring.

^{199}Hg NMR. In the temperature range from $+27$ to -80°C only one ^{199}Hg signal can be detected. At -80°C the half band width of the signal is about 50 Hz, and increases at higher temperatures. This result excludes different bonding modes at different temperatures. The chemical shift of the ^{199}Hg signal, δ -1350 ppm, is

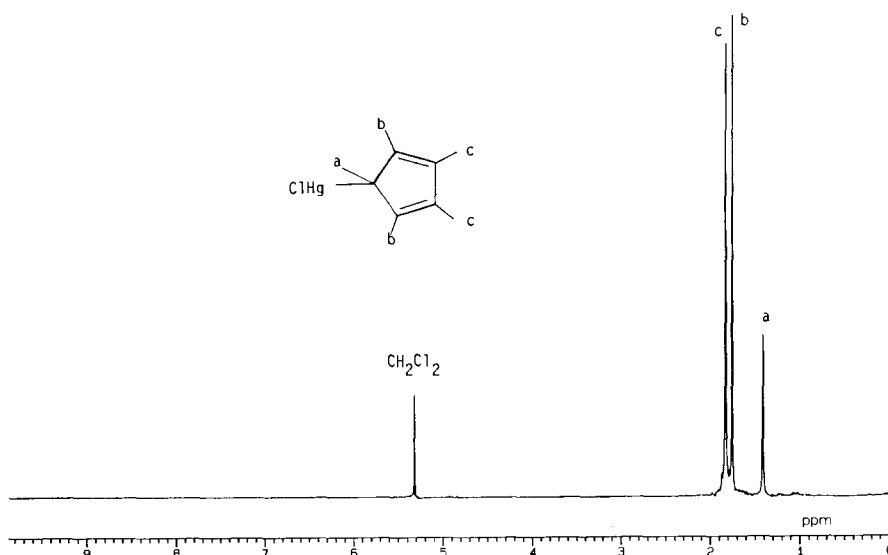


Fig. 1. 400 MHz ^1H NMR spectrum of **2** in CD_2Cl_2 at -80°C .

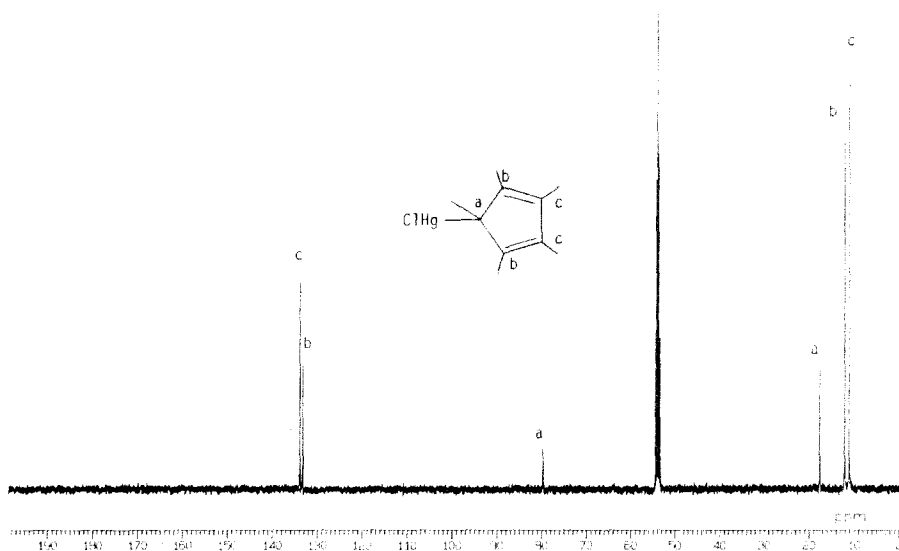


Fig. 2. 100 MHz ¹³C NMR spectrum of **2** in CD₂Cl₂ at -80 °C.

characteristic of η^1 -bonded alkyl or aryl ligands [11] and supports the interpretation of the ¹H and ¹³C NMR data.

Experimental

All operations were conducted under prepurified argon by standard Schlenk techniques. Lithium pentamethylcyclopentadienide was prepared by a published method [7]. Tetrahydrofuran (THF) was purified by distillation under argon from sodium benzophenone, whereas pentane and hexane were distilled under argon from calcium hydride. Microanalyses were performed by the Microanalytical Laboratory, Office of Research Services, University of Massachusetts, Amherst, MA 01003. ¹H, ¹³C and ¹⁹⁹Hg NMR spectra were recorded on JEOL-FX90Q and GX 400 spectrometers.

Pentamethylcyclopentadienylmercuric chloride (2)

A solution of 7.1 g (0.05 mol) of lithium pentamethylcyclopentadienide in 200 ml of THF was added dropwise from a pressure-equalized dropping funnel to 13.5 g (0.05 mol) of mercuric chloride in 200 ml of THF at -78 °C. After the addition was complete, the mixture was allowed to warm slowly to room temperature. The solvent was removed under high vacuum and the resulting yellow residue was extracted several times with warm hexane. The lemon yellow extracts were combined and concentrated under vacuum to ca. one-half of the original volume. Upon cooling at -20 °C, yellow crystals of **2** formed. The product after recrystallization from pentane was obtained in 70% yield (12.6 g). Anal. Found: C, 32.10; H, 4.19; Hg, 53.5. C₁₀H₁₅ClHg calcd.: C, 32.35; H, 4.08; Hg, 54.0%. Mass spectrum: *m/e* 372 (*M*⁺).

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