

FLUORENYL COMPOUNDS OF MERCURY

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SUMMARY

A new method has been developed for the preparation of cyclopentadienyl, indenyl and fluorenyl compounds of mercury which utilizes the reaction of HgCl_2 with the respective $\pi\text{-R}_2\text{ZrCl}_2$ compound in an aqueous-organic medium. The synthesis and properties of fluorenylmercuric chloride and bis(fluorenyl)mercury are described.

INTRODUCTION

Although cyclopentadienyl and indenyl derivatives of mercury have been synthesized and studied in recent years¹⁻⁸, their fluorenyl analogs (in which two benzo groups are fused to the five-membered ring) have not yet been characterized. Attempts by Zimmer and coworkers⁹ to prepare bis(fluorenyl)mercury (Flu_2Hg) in a conventional manner from fluorenyllithium and mercuric chloride were not successful. Only small amounts of 9,9-bifluorenyl were detected, and the authors suggested that Flu_2Hg was possibly not a stable compound. Further attempts by ourselves to synthesize fluorenylmercuric chloride (FluHgCl) or Flu_2Hg from fluorenylsodium and mercuric chloride in either tetrahydrofuran or dimethoxyethane have also been unsuccessful.

We now report a convenient new procedure for the preparation of FluHgCl via a novel metal exchange reaction involving bis(fluorenyl)zirconium dichloride ($\text{Flu}_2\text{ZrCl}_2$) as an intermediary. A facile conversion of FluHgCl to Flu_2Hg is also described, and the properties of both new mercurials are discussed.

RESULTS AND DISCUSSION

Metal exchange reactions in the metallocene area are relatively few in number, and have rarely been used for synthetic purposes. For example, it has long been known that Cp_2Mn and Cp_2Hg react with ferrous chloride in tetrahydrofuran to give ferrocene^{1,10}. $(\text{Cp}_2\text{ZrPh})_2\text{O}$, when treated with thallium sulfate, gives CpTi quantitatively, while an analogous reaction with mercuric chloride results in the

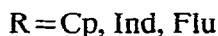
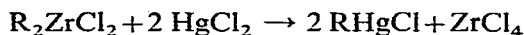
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formation of PhHgCl^{11} . In the course of some recent studies on the properties of zirconocene dichloride (Cp_2ZrCl_2), we observed that when an aqueous solution of the latter (or a suspension of it in ether) was treated with an aqueous solution of mercuric chloride, the well-known compound CpHgCl^4 was formed. Unexpectedly, the same result was obtained in lower yield using titanocene dichloride (Cp_2TiCl_2). Treatment of CpHgCl formed in this way with a saturated aqueous solution of potassium iodide subsequently produced bis(cyclopentadienyl)mercury (Cp_2Hg) in quantitative yield.

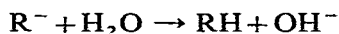
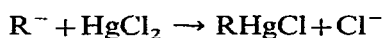
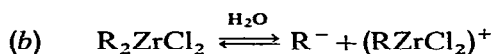
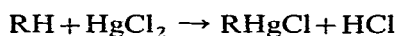
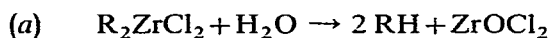
Apart from providing a rapid, facile route to cyclopentadienylmercury compounds from the commercially available Cp_2ZrCl_2 , these methods have proved to be of special utility in the preparation of FluHgCl and Flu_2Hg from $\text{Flu}_2\text{ZrCl}_2$ ¹². Thus, treatment of $\text{Flu}_2\text{ZrCl}_2$ in ether or methylene chloride with an aqueous solution of mercuric chloride results in rapid cleavage of the π -bonded fluorenyl rings*, and the formation of FluHgCl . Small amounts of fluorene are also formed in this reaction. It is of interest to note that water in conjunction with an organic solvent is necessary to promote this metal exchange reaction, since no reaction appeared to occur when anhydrous tetrahydrofuran was used alone as the solvent.

FluHgCl can be easily converted into Flu_2Hg by treatment with aqueous saturated potassium iodide. The procedure is similar to that used to convert indenylmercuric chloride (IndHgCl) into bis(indenyl)mercury (Ind_2Hg)⁶, and is also applicable for the formation of Cp_2Hg from CpHgCl .

Although the mechanism by which this metal exchange reaction proceeds is not yet clear, it seems reasonable to presume from the evidence presently available that it does not take place via a simple metathetical exchange, as in the following:



The fact that the presence of water is necessary leads us to suggest that one of the following pathways is more likely:



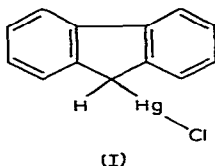
The first mechanism is improbable, since mercuric chloride does not react readily with cyclopentadiene, indene or fluorene. The second mechanism seems to be more reasonable if one assumes that water can provoke a partial ionization of the organic ligand in the zirconium complex to give an anion which can react concurrently with mercuric chloride and with water to give RHgCl and RH , respectively.

* The fluorenyl rings in $\text{Flu}_2\text{ZrCl}_2$ are presumably π -bonded to zirconium, as has been proposed for (fluorenyl)tricarbonylmanganese¹³.

The infrared spectra of FluHgCl and Flu_2Hg are very similar to each other, and differ from the spectrum of fluorene principally in the 850 to 600 cm^{-1} region. Thus, the intense band at 740 cm^{-1} in fluorene¹⁴ which has been ascribed to the C-H bending modes of the six-membered rings is replaced by two major bands of medium and strong intensities at 770 and 730 cm^{-1} , as well as other bands of weaker intensities. Moreover, the band at 690 cm^{-1} which has previously been attributed to the CH_2 rocking modes in fluorene is completely absent in FluHgCl and Flu_2Hg .

The mass spectrum of FluHgCl exhibits the expected molecular ion at m/e 402 (based on ^{35}Cl and ^{202}Hg isotopes). Other major assignable peaks include those at m/e 330 (Flu)₂⁺, 272 (HgCl_2)⁺, 166 (FluH)⁺, and 165 (Flu)⁺.

Although both FluHgCl and Flu_2Hg are relatively insoluble in common organic solvents, an NMR spectrum of the former has been obtained in $\text{DMSO}-d_6$, and is consistent with localized carbon-to-metal σ -bonding (I)*. In addition to aromatic proton absorption between τ 2.0 and 2.8, a sharp singlet resonance due to the methine proton at C-9 is observed at τ 5.18. The relative intensities of these absorptions are approximately 8/1. Kitching *et al.*⁸ have already pointed out that the



methine proton in IndHgCl (τ 5.68 in $\text{THF}-d_8$ ⁸, τ 5.6 in DMSO ⁶) is deshielded compared to the methine proton in the limiting structure of CpHgCl (τ 5.86 in $\text{THF}-d_8$ ¹⁵). Diamagnetic anisotropic deshielding effects imposed by the second aromatic ring evidently result in a further lowering of the methine proton resonance in FluHgCl . Additional studies designed to determine the magnitude of $^{199}\text{Hg}-\text{H}$ spin-spin coupling in these new fluorenyl mercurials are in progress, and will be reported at a later date**.

EXPERIMENTAL

$\text{Flu}_2\text{ZrCl}_2$ was prepared by a reaction between fluorenylsodium and zirconium tetrachloride in dimethoxyethane, following a procedure described earlier¹². Melting points are uncorrected. Microanalyses were carried out by Mr. Charles Meade, Microanalytical Laboratory, Office of Research Services, University of Massachusetts.

Preparation of fluorenylmercuric chloride (FluHgCl)

Into a separatory funnel containing an aqueous solution of 1.0 g (3.7 mmoles) of mercuric chloride was introduced 500 mg (1.0 mmole) of $\text{Flu}_2\text{ZrCl}_2$. Methylene chloride (20 ml) was added, and the suspension was shaken until the orange solid disappeared to give a white crystalline product. This was filtered, washed with ethanol, then ether, and dried. The methylene chloride portion was separated, dried over

* Both FluHgCl and Flu_2Hg would be expected to be stereochemically rigid, since intramolecular rearrangements within the five-membered rings would not be possible.

** Note added in proof. $J(^{199}\text{Hg}-\text{H})$ has now been determined to be 490 Hz for FluHgCl (I).

anhydrous sodium sulfate and concentrated to give more of this product. Evaporation of the solvent produced a small amount of fluorene which was identified by its melting point. The total weight of FluHgCl obtained was 200 mg (25%). An analytical sample was prepared by recrystallization from methylene chloride. (Found: C, 38.97; H, 2.32; Cl, 8.84. $C_{13}H_9ClHg$ calcd.: C, 38.91; H, 2.26; Cl, 8.84%.)

FluHgCl decomposes without melting at 220°. It is sparingly soluble in methylene chloride, chloroform, tetrahydrofuran, and benzene. It appears to be stable indefinitely to air and light. IR spectrum: major bands occur at 1460 s, 1185 w, 1015 w, 940 w, 770 s(sh), 755 m, 748 m, 730 s(sh), and 660 cm^{-1} m.

Preparation of bis(fluorenyl)mercury (Flu₂Hg)

FluHgCl (100 mg, 0.25 mmole) was dissolved in a minimum amount of methylene chloride and shaken in a separatory funnel with 5 ml of a saturated aqueous solution of potassium iodide. The organic layer was then decanted, dried and concentrated to give 20 mg (30%) of a cream-colored solid. An analytical sample was prepared by recrystallization from methylene chloride. (Found: C, 58.68; H, 3.51; Hg, 37.53. $C_{26}H_{18}Hg$ calcd.: C, 58.81; H, 3.42; Hg, 37.78%.)

Flu₂Hg decomposes without melting at 150° and has virtually the same solubility properties as FluHgCl. It appears to be appreciably more stable to light and air than Cp₂Hg or Ind₂Hg. IR spectrum: The band at 1025 cm^{-1} in FluHgCl is shifted to lower frequency (1015 cm^{-1}). The other bands of Flu₂Hg are very similar to those reported above for FluHgCl.

Preparation of cyclopentadienylmercuric chloride (CpHgCl) from Cp₂ZrCl₂

In a typical run, 1.0 g (3.4 mmoles) of Cp₂ZrCl₂ was suspended in 50 ml of ethyl and shaken in a separatory funnel with an aqueous solution of 2.0 g (7.4 mmoles) of mercuric chloride. The ether portion was then separated, dried over anhydrous sodium sulfate, concentrated and cooled to -20° to produce 0.90 g (44%) of CpHgCl, m.p. 95° dec. (reported⁴ m.p. 96-97°). (Found: C, 20.15; H, 1.82; Cl, 11.80, Hg, 66.49. C_5H_5ClHg calcd.: C, 19.94; H, 1.67; Cl, 11.70; Hg, 66.61%.)

When the above reaction product was treated with 5 ml of a saturated solution of potassium iodide and 50 ml of ether, evaporation of the organic layer gave Cp₂Hg in quantitative yield, m.p. 81° (reported³ m.p. 81-83°).

In a manner analogous to that described above for the synthesis of CpHgCl, a reaction between Ind₂ZrCl₂ and mercuric chloride produced a 40% yield of IndHgCl, identified by its melting point and by its infrared spectrum.

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