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## Abstract

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# PROPERTIES AND STRUCTURE OF DICYCLOPENTADIENYLMERCURY

In a number of previous studies (1–3), dicyclopentadienylmercury was regarded as a compound with localized $\sigma$-bonds Hg–C, corresponding to the structure:

[[chemical structural formula: two cyclopentadienyl rings bonded through Hg, with H and Hg substituent lab
(I)

However, some data—in particular, the presence of a single proton-resonance signal observed in the NMR spectrum (2)—do not correspond to a diene structure of the cyclopentadienyl rings in this compound. In the present work we have studied certain chemical and physical properties of dicyclopentadienylmercury.

By the reaction of dicyclopentadienylmercury with mercuric halide salts, we obtained and characterized cyclopentadienylmercury halides: $C_5H_5HgCl$, $C_5H_5HgBr$, and $C_5H_5HgJ$ (4). Cyclopentadienylmercury bromide can be obtained from $C_5H_5HgCl$ by anion replacement. The latter is symmetrized with ammonia in the cold to $(CH_5H_5)_2Hg$. Upon addition of equimolar amounts of hydrohalic acids to a solution of $C_5H_5HgOH$, an anion-exchange reaction is observed; in an excess of acid, hydrolysis occurs. Dicyclopentadienylmercury and cyclopentadienylmercury halides are not hydrolyzed by water. $(C_5H_5)_2Hg$ does not react with $CO_2$; with $FeCl_2$ it forms ferrocene (1).

We have shown (5) that $(C_5H_5)_2Hg$ can be obtained from $C_5H_5Tl$ in tetrahydrofuran in quantitative yield. We were also able to carry out the reverse reaction: $(C_5H_5)_2Hg$ with a solution of TlOH gives $C_5H_5Tl$ in 30% yield. As one of the arguments in favor of structure (I), the authors of previous studies (1,2) cited the interaction with maleic anhydride. However, without detailed study this reaction cannot be used to prove the diene structure of the cyclopentadienyl rings in $(C_5H_5)_2Hg$ (cf. the reaction with $(C_5H_5)_2Co$) (6). We have found that $C_5H_5Tl$, for which a symmetrical structure has been proved (7,8), reacts with maleic anhydride. From the reaction products, bicycloheptenedicarboxylic acid was isolated. Bromination of $(C_5H_5)_2Hg$ and $C_5H_5Tl$ also gives identical reaction products under analogous conditions (9). An aqueous solution of KCN at

20° decomposes $(C_5H_5)_2Hg$, with cyclopentadiene being isolated quantitatively. *n*-Butyl mercaptan completely decomposes $(C_5H_5)_2Hg$ in ether in the cold.

We measured the UV spectra of $C_5H_6$, $(C_5H_5)_2Hg$, $C_5H_5HgCl$, $C_5H_5HgBr$, and $C_5H_5HgJ$ in 95% ethyl alcohol (see Fig. 1). In the spectrum of $(C_5H_5)_2Hg$, two intense absorption bands are observed at 240 and 286 m$\mu$. The intensity of the 240 m$\mu$ band is two orders of magnitude higher than in the spectrum of $C_5H_6$, which is difficult to explain by the ordinary influence of the electropositive Hg atom on the diene chromophore. This, as well as the appearance of absorption in the long-wavelength part of the spectrum at 286 m$\mu$, is similar to the trend of change in the UV spectra on going from $C_5H_6$ to ferrocene (10), which indicates a similar change of the diene chromophore in these compounds in the direction of delocalization of the $\pi$-electrons.

Substantial differences are also observed in the IR spectra of $C_5H_6$ and cyclopentadienylmercury compounds (see Table 1). In the spectra of $(C_5H_5)_2Hg$ and $C_5H_5HgHal$, absorption bands of medium intensity are observed in the region—

regions 1000–1040 and 1410–1460 cm$^{-1}$, characteristic of vibrations of cyclopentadienyl rings in $\pi$-cyclopentadienyls and cyclopentadienyls of metals, and the band at 1520 cm$^{-1}$, characteristic of the spectrum of $C_5H_6$, is absent. The weak bands present in the spectra of cyclopentadienyl mercury compounds

Table 1

| $(C_5H_5)_2Fe$ | $C_5H_5Tl$ | $(C_5H_5)_2Hg$ | $C_5H_5HgCl$ | $C_5H_5HgBr$ | $C_5H_5HgI$ | $C_5H_6$ |
|---|---|---|---|---|---|---|
| 3105 | 3095 | 3090 | 3100 | 3100 | 3105 | 3120 |
| med.3095 | med.17201605 | med.3080 | med.3075 | med.3090 | med.3095 | med.3090 |
| med.3083 | med.1432 | med.3069 | med.2960 | med.3075 | med.3080 | med.3060 |
| med.178017331703765120510[1256]1107[1248]1004 | | | | med.3055 | med.3070 | med.2970 |
| str.[855][844] | str.815753 | med.28802860 | med.17286546101480 | med.2960 | med.2960 | med.2940 |
| str.718 | –735 | med.1383 | med.1376 | med.29252855 | med.17293627654183017 | 3516251460 |
| med.492 | str. | med.1299[1240]1129010848[3110]1084101 | | | med.1378 | med.2895 |
| str.476 | | med.991 | med.991 | med.1377 | med.1292123 | med.26351845181817301630 |
| str. | | med.962 | med.964942 | med.1292123011[818]5 | med.108185710522 | |
| | | med.908 | –938 | med.988 | med.990 | str.14821368 |
| | | str.887 | str.916 | med.956 | med.959 | str.12941239 |
| | | str.822 | med.900 | med.935 | med.925 | med.1089962 |
| | | med.755 | med.820 | str.912 | str.915 | med.926 |
| | | str.644 | med.766 | med.898 | str.904 | med.892 |
| | | str.584 | str.700648 | med.818 | str.822 | str.805 |
| | | | med.567 | med.755 | med.812 | med.756728664 |
| | | | | str.725680650 | med.754 | str. |
| | | | | med.565 | str.722648 | |
| | | | | | med.635 | |
| | | | | | med.565 | |

Designations: str. —strong band, med. —band of medium intensity, without an index —weak band, in brackets —band of very weak intensity.

weak bands in the region 1600-1800 cm$^{-1}$ have no grounds for being assigned to stretching vibrations of $C = C$ bonds. Bands of the same character in this region are observed in the spectra of many $\pi$-cyclopentadienyls of metals. On the basis of a calculation of the vibrations of the cyclopentadienyl rings of ferrocene $^{(11)}$, it was shown that these bands correspond to overtones and combination frequencies. In the region of stretching vibrations of $C—H$ bonds in the spectra of $(C_5H_5)_2Hg$ and $C_5H_5HgHal$, in contrast to the spectra of $(C_5H_5)_2Fe$ and $C_5H_5Tl$, two groups of frequencies are observed, at 2960 and 3070-3100 cm$^{-1}$. However, in the spectra of such $\pi$-cyclopentadienyls of metals as $(C_5H_5)_2Ni$ $^{(12)}$ and $(C_5H_5)_2Pb$ $^{(13)}$, two groups of frequencies are likewise present in this region. Without taking into account the symmetry of the molecule and calculating the forms of the normal vibrations, the region of stretching vibrations of $C—H$ bonds in IR spectra cannot be used to prove the presence of nonequivalent

protons in the molecule. Much more reliable information for such judgments can be obtained from consideration of NMR spectra.

In the high-resolution NMR spectrum of dicyclopentadienylmercury only one proton-resonance signal is observed, without any signs of fine structure, at $5.15 \cdot 10^{-6}$, whereas in the high-resolution NMR spectrum of $C_5H_6$ ($^{14}$) two signals with fine structure were found: a multiplet at 6.38 and a multiplet with 5 maxima at $2.79 \cdot 10^{-6}$, with an area ratio of the signals of $4 : 2$. Both in the character of the NMR spectrum and in the magnitude of the chemical shift, the position of the proton signal of $(C_5H_5)_2Hg$ is much closer to the position of the signals of the protons of metal $\pi$-cyclopentadienyls ($4.1—5.0 \cdot 10^{-6}$) than to the signals of protons at double bonds in cyclopentadiene ($6.38 \cdot 10^{-6}$).

Thus, many of the arguments given in the literature in favor of formula (I) cannot be considered convincing. A number of data obtained by us in studying the chemical properties and the UV, IR, and NMR spectra indicate the absence of a diene structure and the equivalence of the protons of the cyclopentadienyl rings in the molecule $(C_5H_5)_2Hg$. The reaction of $(C_5H_5)_2Hg$ with TlOH, with formation of $C_5H_5Tl$, has no analogies in the chemistry of organomercury compounds. The decomposition of $(C_5H_5)_2Hg$ under the action of KCN and $C_4H_9SH$ reveals a high lability of the metal–ring bond in $(C_5H_5)_2Hg$. The increased number of frequencies in the IR spectra of cyclopentadienyl compounds of mercury as compared with the spectra of $(C_5H_5)_2Fe$ and $C_5H_5Tl$, although it indicates different symmetry of the structures of $(C_5H_5)_2Fe$ and $(C_5H_5)_2Hg$, does not exclude the possibility of interaction of the conjugated $\pi$-electron system of the cyclopentadienyl rings with the mercury atom, similar to that recently found in $\pi + \sigma$ complexes of mercury rhodanides with benzene of the type $MeHg_2(SCN)_6 \cdot C_6H_6$ ($^{15}$).

**Fig. 1.** UV spectra of cyclopentadienyl mercury compounds: $I$ $-C_5H_5HgBr$; $II$ $-C_5H_5HgJ$; $III$ $-(C_5H_5)_2Hg$; $IV$ $-C_5H_5HgCl$; $V$ $-C_5H_6$.

Fig. 1. UV spectra of cyclopentadienyl mercury compounds: I –C5H5HgBr; II –C5H5HgJ; III –(C5H5)2Hg; IV –C5H5HgCl; V –C5H6

Figure 1: Fig. 1. UV spectra of cyclopentadienyl mercury compounds: I –C5H5HgBr; II –C5H5HgJ; III –(C5H5)2Hg; IV –C5H5HgCl; V –C5H6

**Preparation of $C_5H_5Tl$ from $(C_5H_5)_2Hg$.** To a solution of 0.625 g of $Tl_2SO_4$ and 0.25 g of KOH in 15 ml of water and 15 ml of methanol was added a solution of 0.35 g of $(C_5H_5)_2Hg$ in 15 ml of methanol at $0 \pm 2^{\circ}$; the mixture was stirred for 30 min, the precipitate was filtered off, washed with water, methanol, and benzene, dried in air, and sublimed in vacuo at 90—110°/1 mm Hg. $C_5H_5Tl$, weight 0.18 g, yield 31%.

$C_5H_5Tl$. Found, %: C 22.67, 22.59; H 2.17, 1.98; Tl 75.07, 74.90
Calculated, %: C 22.32; H 1.86; Tl 75.82

**Preparation of $C_5H_5HgCl$.** To a solution of 0.165 g of $(C_5H_5)_2Hg$ in 5 ml of THF was added 0.135 g of $HgCl_2$ in 5 ml of THF; the solvent was removed, the residue dried in vacuo and recrystallized from abs. ethanol without heating. $C_5H_5HgCl$, m.p. 96–97°, molecular weight found 196 (dioxane, cryoscopy), calculated 301. The substance is stable at room temperature.

$C_5H_5HgCl$. Found, %: C 19.74, 19.64; H 1.71, 1.48; Hg 66.14; Cl 11.96, 11.98
Calculated, %: C 19.95; H 1.67; Hg 66.60; Cl 11.78

Analogously, $C_5H_5HgBr$ was obtained. Decomp. temp. 78-80°;

| | |
|---|---|
| Found, %: | C 17.62, 17.58; H 1.58, 1.69; Br 23.25, 23.40 |
| $C_5H_5HgBr$. Calculated, %: | C 17.43; H 1.46; Br 23.10 |

and also $C_5H_5HgI$, bright-yellow crystals, decomp. temp. 80-90°, slightly subliming at about 60°. Store in the cold.

| | |
|---|---|
| Found, %: | C 15.75, 15.31; H 1.41, 1.22; Hg 50.82, 59.77; I 32.34, 32.16. |
| $C_5H_5HgI$. Calculated, %: | C 15.30; H 1.28; Hg 51.00; I 32.33 |

**Preparation of $C_5H_5HgBr$ from $C_5H_5HgCl$.** 0.18 g of $C_5H_5HgCl$ in a 1:1 aqueous-acetone solution was treated for 30 min with moist neutral $Ag_2O$ (from 0.5 g of $AgNO_3$); fresh $Ag_2O$ was added (from 0.5 g of $AgNO_3$), treatment was continued for another 30 min, the precipitate was filtered off, the solution was neutralized with several drops of HBr acid, the precipitate was filtered off, washed with ice water, and dried in vacuum. $C_5H_5HgBr$, weight 0.07 g. Found, %: C 17.46, 17.42; H 1.56, 1.51.

**Symmetrization of $C_5H_5HgCl$.** 0.4 g of $C_5H_5HgCl$ was dissolved in 20 ml of benzene, a stream of dry $NH_3$ was passed through for 1 min, the precipitate was filtered off, the benzene was removed, and the residue was recrystallized from ether without heating. $(C_5H_5)_2Hg$, m.p. 81-83°, weight 0.15 g, yield 68%.

**Reaction of** $(C_5H_5)_2Hg$ **with KCN.** In a 10-ml Favorskii flask connected to a trap cooled to −80°, 0.33 g of $(C_5H_5)_2Hg$ and 3 ml of 10% aqueous methanol were placed; from a dropping funnel a saturated aqueous solution of 2.5 g of KCN (10-fold excess) was added, and a stream of $N_2$ was passed for 7–8 h. To the contents of the trap was added 10 ml of 10% aqueous methanol; at 10° it was treated with alkaline TlOH solution (from 30 g of $Tl_2SO_4$); the precipitate was filtered off, washed with water, and dried in air. 0.54 g of $C_5H_5Tl$ was obtained, yield close to quantitative.

**Reaction of** $(C_5H_5)_2Hg$ **with** $C_4H_9SH$**.** 0.0350 g of $(C_5H_5)_2Hg$ was dissolved in ether, 10 drops of *n*-butyl mercaptan (excess) were added, and after 15 min the precipitate was filtered off, washed with ether, and dried. Weight of $(C_4H_9S)_2Hg$ 0.04 g, m.p. 85–86° (from alcohol).

| | |
|---|---|
| Found, %: | C 24.83; H 4.51 |
| $C_8H_{18}S_2Hg$. Calculated, %: | C 25.35; H 4.79 |

**Spectral measurements.** The UV spectra of the substances studied were measured in 95% ethyl alcohol in the region 205–400 m$\mu$ on an EPS-2 “Hitachi” recording spectrophotometer. IR spectra were recorded on a UR-10 double-beam IR spectrometer in the region from 400 to 4000 cm$^{-1}$, with KBr, NaCl, and LiF prisms, in crystals with Vaseline oil and fluorinated hydrocarbons and in films from absolute benzene and tetrahydrofuran. The NMR spectrum of $(C_5H_5)_2Hg$ was recorded in absolute benzene on a JNH4H100 NMR spectrometer (100 MHz)* (standard $(CH_3)_4Si$).

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*Note: Figure translations are in progress. See original paper for figures.*