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Note

The reaction of ferrocene with mercuric chloride revisited: ‘$Cp_2Fe*2HgCl_2$’ = $[(C_5H_5)Fe(C_5H_4HgCl)]_2[Hg_2Cl_6]$, comparison of its molecular structure with that of chloromercuriferrocene

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Abstract

The ‘blue adduct’ formed from the decomposition of the red ‘$Cp_2Fe*7HgCl_2$’ and formulated as ‘$Cp_2Fe*2HgCl_2$’ was characterized by X-ray crystallography as the ring-mercurated ferricenium salt $[(C_5H_5)Fe(C_5H_4HgCl)]_2[Hg_2Cl_6]$. For comparison, the neutral $[(C_5H_5)Fe(C_5H_4HgCl)]$ was also studied by single-crystal diffractometry. Both compounds have the HgCl group within the plane of the cyclopentadienyl ring with no Fe–Hg interaction. © 2001 Elsevier Science B.V. All rights reserved.

Keywords: Ferrocene; Ferricenium; Mercury; Crystal structures

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1. Introduction

Soon after the discovery of the high activity of the ferrocene molecule in electrophilic aromatic substitution reactions, it was found in 1954 that treatment of ferrocene with mercuric acetate/lithium chloride gave a mixture of $(C_5H_5)Fe(C_5H_4HgCl)$ (**1**) and $(C_5H_4HgCl)_2Fe$ (**2**) [1]. The use of the weaker electrophile $HgCl_2$ was apparently studied only 20 years later and led either to ‘adducts’ of composition ‘$Cp_2Fe*7HgCl_2$’ [2] or ‘$Cp_2Fe*6HgCl_2$’ [3] or to the ferricenium salt $[(C_5H_5)_2Fe]_2[HgCl_4]$ [4], depending on the reaction conditions. The adducts were reported to be unstable and to decompose to blue species, formulated either as ‘$Cp_2Fe*2HgCl_2$’ [2] or as $[Cp_2Fe]_2Hg_2Cl_4$ [5]. Similar reactions with ruthenocene led to crystals of ‘$Cp_2Ru*HgBr_2$’ and ‘$2Cp_2Ru*3HgCl_2$’, which were shown by XRD experiments to contain Ru–Hg bonds [6]. It was therefore concluded that the primary adducts of ferrocene contained Fe–Hg bonds, but there was no crystallographic proof of this assumption.

The formation of species with an iron–mercury bond as the first step in the ring-mercuration reaction of ferrocene was shown to be most likely by recent DFT calculations [7]. The adduct $[(C_5H_5)(C_5H_4HgOCOCF_3)Fe]*Hg(OCOCF_3)_2$ could be isolated in the reaction of ferrocene with $Hg(OCOCF_3)_2$ in toluene [8], and we wondered if similar species were formed in the reactions with $HgCl_2$. We decided, therefore, that it was worthwhile to try to obtain X-ray-quality crystals of some of the strange ‘$HgCl_2$ adducts’ mentioned before.

2. Results and discussion

When ferrocene is stirred with approximately 3.5 equivalents $HgCl_2$ in ether solution according to the procedure given by Hendrickson [2], the red adduct $Cp_2Fe*7HgCl_2$ precipitates in 53% yield (rel. $HgCl_2$). All attempts to obtain crystals from acetone or DMSO solution were unsuccessful due to rapid decomposition to blue or yellow powders or solutions. Evaporation of a saturated aqueous solution (best prepared after keeping the solid 1:7 adduct at room temperature for a while, otherwise hardly anything dissolves) in air gave

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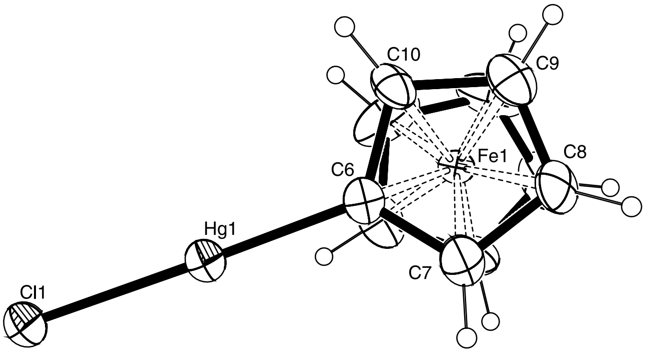

Fig. 1. Molecular structure of the cation $[(C_5H_5)Fe(C_5H_4HgCl)]^+$ of compound **3**.

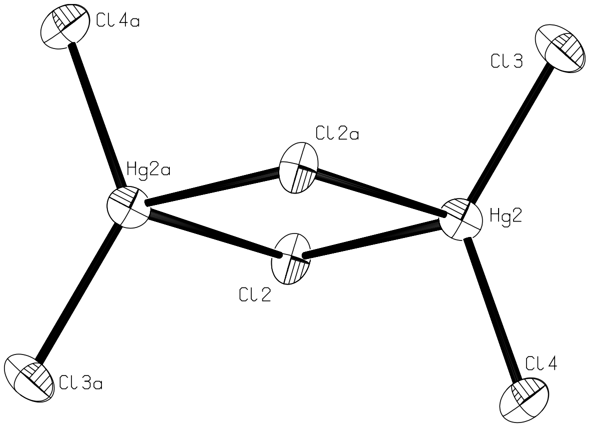

Fig. 2. Molecular structure of the anion $[Hg_2Cl_6]^{2-}$ of compound **3**.

blue crystals of 'Cp_2Fe*$2HgCl_2$', together with some orange and white microcrystals. Mass spectroscopic (EI) investigation of this solid showed the presence of $HgCl_2$ and ferrocene, together with '$C_{10}H_8Cl_2FeHg$', $[(C_5H_5)(C_5H_4HgCl)Fe]$, $[(C_5H_5)Hg(C_5H_4Cl)]$ and $[(C_5H_5)_2Hg]$, which had not been reported before as reaction products.

One of the blue crystals was mounted on a diffractometer and data were collected. Although the dataset was not of a very high quality due to absorption problems, the structure could be solved in the triclinic space group *P*-1 and the compound identified as $[(C_5H_5)(C_5H_4HgCl)Fe]_2[Hg_2Cl_6]$ (**3**)[1]. The structure of the cation is shown in Fig. 1 and that of the anion in Fig. 2.

The $[Hg_2Cl_6]$ anion of **3** can be described as two severely distorted edge-sharing tetrahedra generated by a crystallographic inversion center from an $HgCl_3$ group. The Hg–Cl bonds vary from ca. 2.32 Å for the terminal to 2.54 and 2.81 Å for the bridging groups. Similar distorted geometries have been observed before in chloromercurate structures [10].

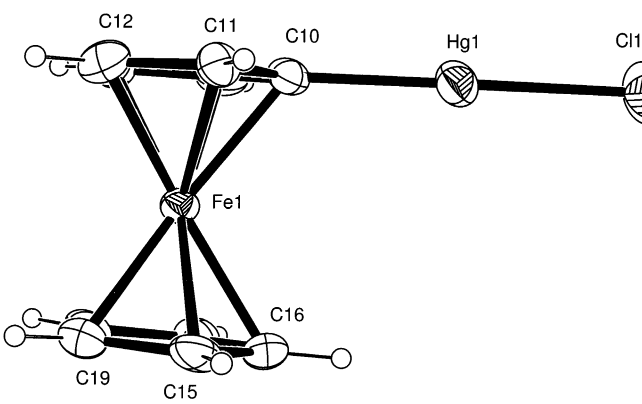

Fig. 3. Molecular structure of the eclipsed form of $[(C_5H_5)Fe(C_5H_4HgCl)]$ (molecule 1 of compound **1**).

Since the cation of **3** is the oxidized form of chloromercuriferrocene (**1**), the structure of which has not been reported before (to the best of our knowledge)[2], we examined the crystal structure of this compound, too. Compound **1** crystallizes in the triclinic space group *P*-1, however, with two independent molecules in the unit cell (one with staggered, and one with eclipsed conformation). Fig. 3 shows the structure of molecule 1.

In both compounds, the cyclopentadienyl rings deviate only slightly from planarity, and the interplanar angles of $2 \pm 0.6°$ show that they are parallel to each other. The distances of the iron atoms from the ring planes (and from the single carbon atoms) are slightly larger in the ferricenium complex **3** than in the neutral complex **1**, as it is always observed, and — within the 2σ-limit — there is no difference between the distances to the substituted and the unsubstituted ring.

The mercury substituent is shifted more out of the ring plane away from the iron in **3**, than in **1**, which leads to Fe–Hg distances of 3.63–3.70 Å. These exclude any metal–metal interactions, although they are significantly shorter than the derived 3.870–3.996 Å obtained from DFT calculations for $[FeCp(C_5H_4)Hg]^+$ [7]. Within the accuracy of the measurement, the carbon–mercury distances are the same in both compounds and are again much shorter (>0.25 Å) than those obtained in the DFT calculations. However, the Hg–Cl distance is longer (by 5σ) in **1** than in **3** with the C–Hg–Cl angle deviating slightly more from linearity.

Due to the limited accuracies of the measurements, it cannot be concluded if the differences between the individual C–C and Fe–C distances are of any relevance. The averaged values of the C–C distances are slightly larger for the neutral **1**.

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[1] This compound had been obtained before by reaction of $[(C_5H_5)Fe(C_5H_4BPh_3)]$ with $HgCl_2$ [9].

[2] Several crystal structure determinations of cyclometallated ferrocenylimines with HgCl substituents [11] and the structure of $[(1\text{-}HgCl)(2\text{-}CH_2NMe_2)(H_3C_5)Fe(C_5H_5)]$ [12] have been reported.

Table 1
Important distances and angles in **1** and **3** [a]

	Compound **1** (mol. I)	Compound **1** (mol. II)	Compound **3**
Rms Δ (Cp–Hg) (Å)	0.0072	0.0051	0.0024
Rms Δ (Cp–H) (Å)	0.0050	0.0043	0.0027
D {Fe–(Cp–Hg)} (Å)	1.648 (5)	1.643 (6)	1.688 (5)
D {Fe–(Cp–H)} (Å)	1.653 (5)	1.652 (6)	1.694 (5)
D {Hg–(Cp–Hg)} (Å)	−0.028 (17)	0.039 (20)	−0.058 (18)
r(Hg–C) (Å)	2.045 (11)	2.031 (11)	2.042 (10)
r(Hg–Cl) (Å)	2.312 (3)	2.331 (3)	2.298 (3)
∠ (C–Hg–Cl) (°)	177.0 (3)	177.7 (3)	178.7 (3)
r(Hg–Fe) (Å)	3.66	3.63	3.70
R_{av} (Fe–C_{cpHg}) (Å)	2.040 (5)	2.041(5)	2.073 (5)
R_{av} (Fe–C_{cpH}) (Å)	2.046 (5)	2.033 (6)	2.072 (5)
R_{av} $(C–C)_{cpHg}$ (Å)	1.413 (7)	1.423 (7)	1.413 (7)
R_{av} $(C–C)_{cpH}$ (Å)	1.419 (8)	1.391 (9)	1.399 (9)

[a] (Cp–Hg) symbolizes the mercury substituted ring, (Cp–H) the unsubstituted ring. Rms Δ means root-mean-squared deviation from planarity. *D* symbolizes the distance of an atom from a plane, *r* the distance of two atoms, R_{av} stands for the average distance from Fe to the Cp-carbon atoms or the average C–C bond length within a Cp ring.

In general, the geometry around the C–Hg–Cl group is very similar to the situation found in the known ring-mercurated ferrocenylimines (except for the missing nitrogen donor ligand): in these compounds the C–Hg bonds vary from 2.016 to 2.037 Å and the Hg–Cl bonds from 2.296 to 2.314 Å, while the C–Hg–Cl bond angles are between 176.8 and 179.1° [11].

Table 1 collects the most important structural features of **1** and **3**, while Table 2 contains the experimental data for the structure determinations.

3. Conclusions

The isolation and structural characterization of **3** shows that mercuration of the cyclopentadienyl ring of ferrocene also occurs with $HgCl_2$. However, there are obviously several decomposition pathways open to the 1:7 adduct. This can be concluded from the observation of Traverso et al. who, by photolysis of the 1:7 adduct at 364 nm, obtained the dimer $[Cp_2Fe]_2Hg_2Cl_4$, with "no evidence indicating the presence of HgCl bonded to a cyclopentadienyl ring" [5]. Likewise, the occurrence of a bis-cyclopentadienyl-mercury species in the mass spectrum indicates the formation of even more complex products, perhaps dimers or oligomers with Hg bridges between two ferrocenyl moieties. Thus, our studies have brought some light to this chemistry, but there are still several issues to be addressed in further studies.

4. Experimental

From 2.00 g ferrocene (10.8 mmol) and 10.0 g $HgCl_2$ (36.8 mmol) in 100 ml Et_2O, 5.86 g '$Cp_2Fe*7HgCl_2$' (2.8 mmol) can be isolated as a brown-red powder. The ^1H-NMR spectrum of a freshly prepared solution in acetone-d_6 shows a very broad singlet resonance at δ

Table 2
Experimental details of the crystal structure determinations of **1** and **3**

	Compound **1**	Compound **3**
Empirical formula	$C_{10}H_9ClFeHg$	$C_{10}H_9Cl_4FeHg_2$
Formula weight	421.06	728.00
Temperature (K)	293(2)	293(2)
Crystal system	triclinic	triclinic
Space group	*P*-1	*P*-1
Unit cell dimensions		
a (Å)	7.6650(10)	7.378(2)
b (Å)	9.4970(10)	9.7490(10)
c (Å)	14.3290(10)	10.942(2)
α (°)	75.160(10)	91.340(10)
β (°)	87.710(10)	96.05(2)
γ (°)	83.520(10)	107.230(10)
V ($Å^3$)	1001.77(18)	746.3(3)
Z	4	2
Absorption coefficient (mm^{-1})	16.965	22.169
Crystal size (mm)	0.20 × 0.13 × 0.025	0.15 × 0.10 × 0.08
Theta range for data collection (°)	2.23–25.00	2.19–25.00
Index ranges	±*h*, ±*k*, ±*l*	+*h*, ±*k*, ±*l*
Reflections collected	6968	3269
Independent reflections	3487 (R_{int} = 0.0252)	2615 (R_{int} = 0.0337)
Absorption correction	DIFABS	DIFABS
Max/min transmission	0.567, 0.103	0.66, 0.19
Data/parameters	3487/235	2615/154
Goodness-of-fit on F^2	1.015	1.016
R_1 $[I>2\sigma(I)]$	0.0469	0.0350
wR_2 (all data)	0.1260	0.0937
Largest difference peak and hole (e $Å^{-3}$)	2.030 and −2.311	1.591 and −1.686

4.48 ppm. AAS/ICP measurements confirm the proposed 1:7 stoichiometry: Hg, 67.4%, Fe, 2.8%; Calc. for $C_{10}H_{10}Cl_{14}FeHg_7$: Hg, 67.3%, Fe, 2.7%.

Keeping the solid adduct for 2 weeks under nitrogen in the dark does not prevent a color change to blue. Dissolving this bluish powder in water and slow evaporation in air gives blue crystals together with orange and white microcrystals.

Mass spectrum (EI): $m/z = 456$ ($C_{10}H_8Cl_2FeHg$), 422 ($C_{10}H_9ClFeHg$), 364 ($C_{10}H_9ClHg$), 329 ($C_{10}H_{10}Hg$), 272 ($HgCl_2$), 237 (HgCl), 202 (Hg), 186 ($C_{10}H_{10}Fe$), 121 (C_5H_5Fe).

One of them was mounted with epoxy glue on top of a glass fiber and measured on a Siemens P4 four-circle diffractometer (293 K, Mo–K_α radiation with graphite monochromator). The structure was solved with SHELXS-86 and refined with SHELXL-93 and SHELXL-97, using full matrix-least squares methods. A psi-scan dataset was measured, but the use of the XEMP routine of SHELXTL-Plus produced a lower quality *hkl*-file than could be obtained by use of the DIFABS routine, which was therefore used.

Commercially available chloromercuriferrocene (Aldrich) was recrystallized from chloroform and yielded X-ray-quality crystals, which were measured under analogous conditions as **3**. The same programs were used for structure solution and refinement. Since the same problems were encountered with the absorption correction, DIFABS was also used in the refinement.

5. Supplementary material

Crystallographic data for the structural analysis have been deposited with the Cambridge Crystallographic Data Centre CCDC no. 154694 for compound **1** and CCDC no. 154695 for compound **3**. Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (Fax: +44-1223-336033; e-mail: deposit@ccdc.cam.ac.uk).

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