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Synthesis and structure of the first bromide complex of the four-mercury anticrown $[(o,o'\text{-}C_6F_4C_6F_4Hg)_4Br]^-$

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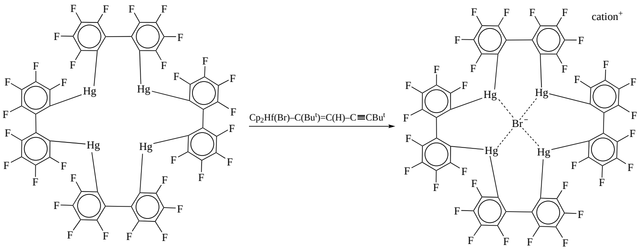
The first bromide complex of the tetramercury anticrown, $[(o,o'\text{-}C_6F_4C_6F_4Hg)_4Br]^-(PyH)^+$, was synthesized by the reaction of alkenyl bromide complex of hafnocene $Cp_2Hf(Br)\text{–}C(Bu^t)\text{=}C(H)\text{–}C{\equiv}CBu^t$ with cyclic tetrameric perfluoro-*o,o'*-biphenylenemercury $(o,o'\text{-}C_6F_4C_6F_4Hg)_4$. The structures of the obtained complex and initial alkenyl bromide complex were studied by the X-ray diffraction analysis.

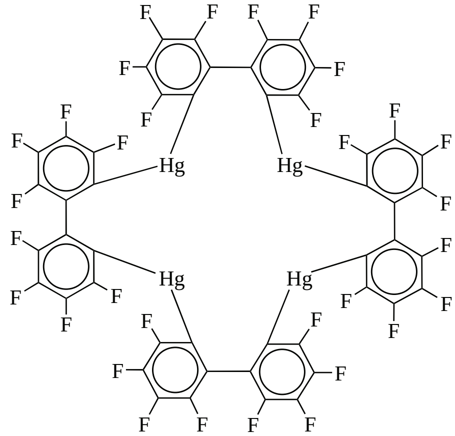


Keywords: anticrown compounds, metallacyclocumulene, complexation, mercury, hafnium, bromide.

The discovery of the fact that the activity of the Ziegler catalysts based on Group 4 metallocene dihalides and aluminium alkyls in the olefins polymerization is due to $[Cp'_2MR]^+$ cationic complexes was among the remarkable achievements of chemistry. Such type of cations can be obtained in the individual state by the reaction of dialkyl or dibenzyl derivatives of titanocene, zirconocene, and hafnocene with strong Lewis acids, *e.g.*, $B(C_6F_5)_3$, Ph_3C^+ (Scheme 1, for example, reviews[1–4]).

The catalytic activity of these cationic metallocenes in polymerization crucially depends on their electrophilicity, which, in turn, is largely determined by the nature of the counter anion and the nature of the solvents.

In the present work we decided to use principally new class of Lewis acids such as anticrowns (*e.g.*, macrocycles **1**–**9**) for the preparation of the Ziegler catalysts as interesting and promising direction of research. Such a choice was made due to the fact that



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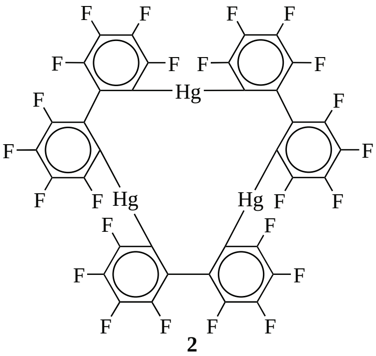

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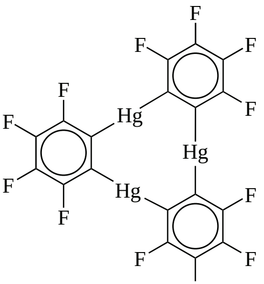

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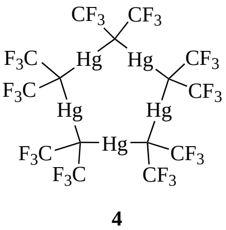

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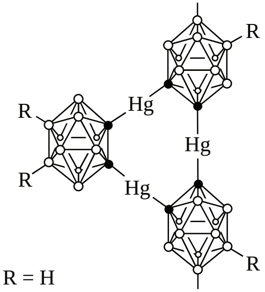
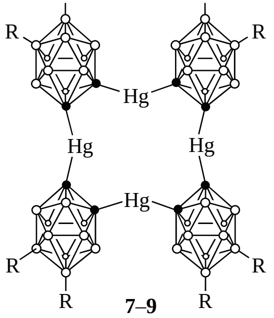


5 R = H
6 R = Me
5, **6**



7–**9**

7 R = H
8 R = Me
9 R = Et

$$\mathrm{Cp'_2MR_2} + \mathrm{AX}_n \longrightarrow [\mathrm{Cp'_2MR}]^+ [\mathrm{AX}_n\mathrm{R}]^-$$

$$\mathrm{M = Ti, Zr, Hf} \qquad \mathrm{AX}_n = \mathrm{B(C_6F_5)_3, Al(C_6F_5)_3, Ph_3C^+}, \textit{etc.}$$

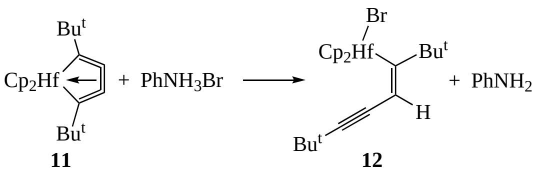
Scheme 1

mercury anticrowns are able to form stable complexes with anions, especially with halides.[5–11]

In the present work, a known[9] cyclic tetrameric perfluoro-*o*,*o*′-biphenylenemercury (*o*,*o*′-$C_6F_4C_6F_4Hg)_4$ **1** was used as an anticrown. To access this compound, a chloride complex [Li(12-crown-4)$_2$]{[(*o*,*o*′-$C_6F_4C_6F_4Hg)_4$]Cl} **10** has recently been obtained in which the chloride anion was located inside the mercuramacrocycle cavity and was nearly symmetrically coordinated by all four mercury centres of the anticrown.[9] This kind of coordination makes the halide anion difficult to be attacked by bulky electrophilic particles, including cationic metallocenes. One may assume that the formation of the bromide complex would be particularly favourable not only due to cooperative coordination by soft Lewis acidic mercury atoms, but also due to the greater softness of the bromide anion itself, while Group 4 metallocenes are hard Lewis acids. Moreover, according to X-ray study of **10**, the slightly larger bromide anion may be more consistent with the size of the anticrown cavity than chloride anion.

Bromide alkenyl complex of hafnocene **12** was obtained by protolysis of the hafnacyclocumulene complex **11** (see refs. 12, 13) with one equivalent of aniline hydrobromide in pyridine at 20 °C (Scheme 2). Complex **12** was isolated in 47% yield and fully characterized. Similar zirconocene monochloride complexes have been described recently.[14,15]

The asymmetric unit of **12** contains two independent molecules (**12A** and **12B**) close in their geometrical characteristics. The structure of **12A** is shown in Figure 1,[†] from which it follows that during the protolysis of **11** the proton attacks cyclopropene carbon atom with C≡CBu^t substituent of the hafnacyclopropene resonance form of the starting complex.[14] It is interesting that metal atom in **12** is bonded to the C(1) atom of the double bond C(1)–C(2) of the enyne moiety and is located *trans* to hydrogen atom at the C(2) atom. The Cp_2Hf unit in **12** has a structure of a bent sandwich and the enyne fragment, hafnium and bromine atoms are located in the bisector plane of the dihedral angle between the η^5-C_5H_5 rings. The lengths of double C(1A)–C(2A) bond and the triple C(3A)–C(4A) bond in the enyne fragment are 1.355(3) and 1.197(3) Å, respectively. The central bond length of the enyne is 1.441(3) Å. The corresponding bond angles at the sp-hybridized carbon atoms are close here to 180° [C(2A)–C(3A)–C(4A) 174.5(3)° and C(3A)–C(4A)–C(5A) 176.4(3)°].



Scheme 2

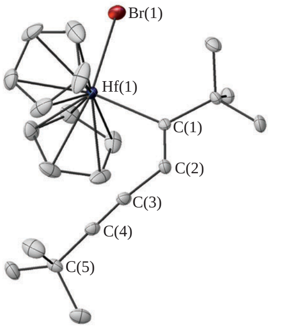


Figure 1 ORTEP representation of the molecular structure of complex **12A** with thermal ellipsoids drawn at the 30% probability level. The hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (°): Hf(1A)–Br(1A) 2.6098(3), Hf(1A)–C(1A) 2.336(2), C(1A)–C(2A) 1.355(3), C(2A)–C(3A) 1.441(3), C(3A)–C(4A) 1.197(3), Hf(1A)–C(1A)–C(2A) 122.11(16), C(1A)–C(2A)–C(3A) 128.0(2), C(2A)–C(3A)–C(4A) 174.5(3), C(3A)–C(4A)–C(5A) 176.4(3).

Then, we proceeded the reaction of tetrameric perfluoro-*o*,*o*′-biphenylenemercury **1** with the obtained alkenyl complex of hafnocene monobromide **12** (Scheme 3) in pyridine at 60 °C with an equimolar ratio of the reactants. Under these conditions, the interaction of the mercury macrocycle with the hafnium complex was detected, which was seen from the changes in the ^{19}F NMR spectra. After cooling to room temperature and concentrating the reaction solution, colourless crystals of the new substance were obtained.

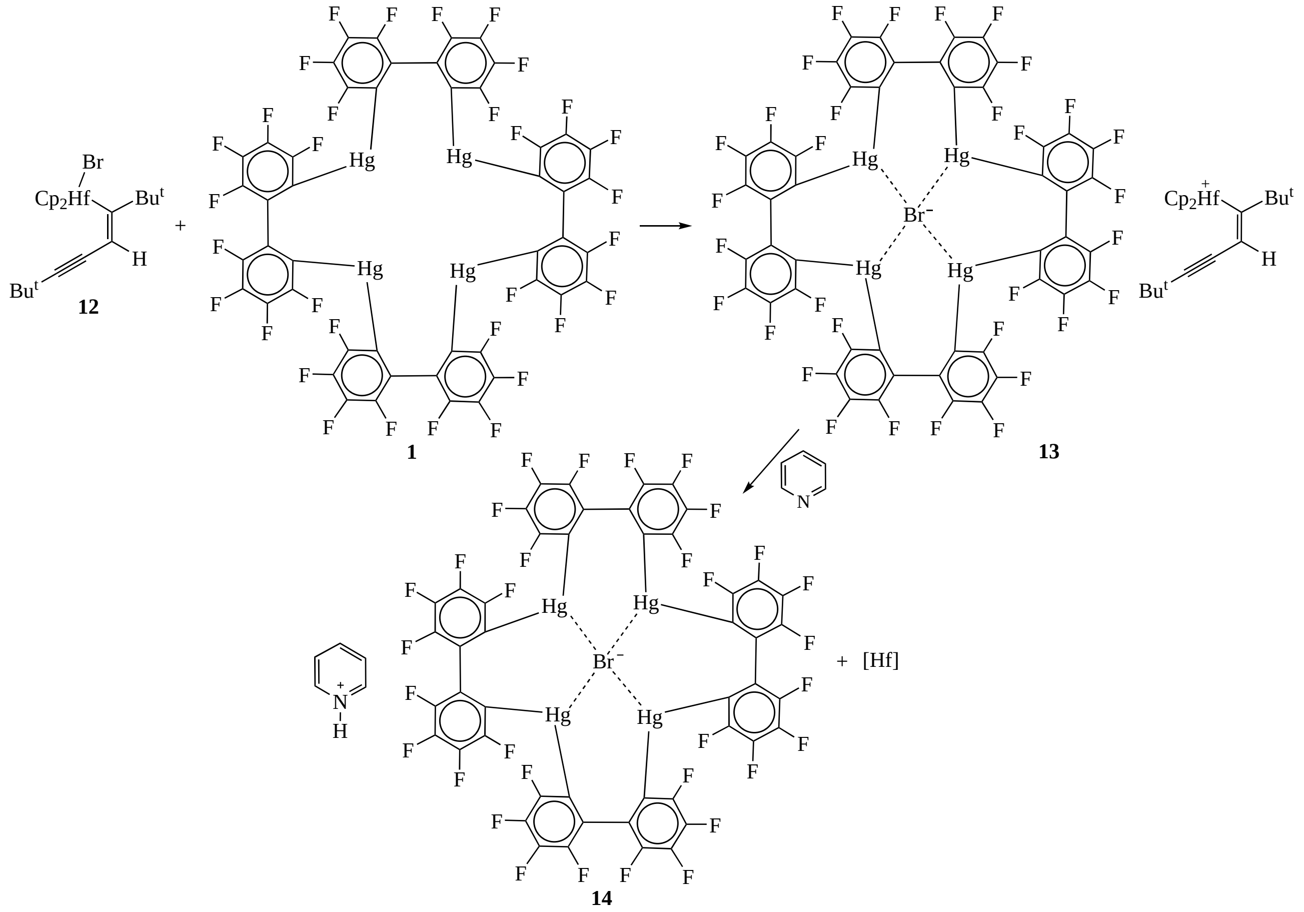
According to an X-ray analysis, it turned out that instead of the expected anionic bromide complex of mercuracycle **1** with enyne counter cation **13**, a complex with pyridinium counter cation **14** was formed as a result of the above-mentioned reaction. It can be assumed that the proposed hafnocenium cation in complex **13** is apparently unstable under these conditions and would quickly decompose because of the strong binding of the bromine atom of **12** by anticrown and as a result of its elimination in the form of a bromide anion and the impossibility of stabilizing the resulting cation by steric hindrance. As a consequence, complex **14** is formed where pyridinium acts as a cation. ^{1}H NMR spectrum of the reaction mixture contains a large number of difficult to interpret signals which also points to the decomposition of the hafnium part. It is noteworthy that compound **14** can also be obtained directly from anticrown **1** and pyridinium bromide in acetone–ethanol mixture.

The molecular structure of complex **14** is shown in Figure 2.[†] The projection of anionic part of **14** perpendicular the *c* axis of the crystal is shown in Figure S1 (see Online Supplementary Materials). In this compound, bromide ligand is located in the anticrown cavity like chloride in **10**[9] and is also η^4 bonded with all its mercury centres, but at the same time it significantly deviates from the mean plane of four mercury atoms of the macrocyclic host by 0.728(2) Å (in the case of chloride in **10** by 0.79 Å) towards the pyridinium cation forming a weak hydrogen bond with it [N(1)···Br(1) 3.307(15) Å, N(1)–H(1A)···Br(1) 144°]. The Hg–Br bond lengths in this adduct are 3.1276(4) and 3.3191(4) Å (*av.* 3.223 Å), and all these distances are considerably shorter than the sum of the van der Waals radii of mercury (1.73–2.00 Å,[16,17] 2.1 Å[18]) and bromine (1.9 Å[18]) atoms. In the above-mentioned chloride adduct **10**, the Hg–Cl bond lengths varied in the range of 2.9221(14)–3.0205(15) Å

[†] *Crystal data for* **12**. $C_{22}H_{29}BrHf$ (M = 551.85 g mol^{-1}), triclinic, space group $P\bar{1}$, a = 11.2818(4), b = 13.8692(5) and c = 14.3460(5) Å, V = 2075.14(13) Å^3, Z = 4, T = 120 K, μ(MoK$_\alpha$) = 6.953 mm^{-1}, d_{calc} = 1.766 g cm^{-3}, 28128 reflections measured (2.97° ⩽ 2θ ⩽ 61.448°), 12763 unique (R_{int} = 0.0227, R_{sigma} = 0.0324) which were used in all calculations. The final R_1 was 0.0224 [$I > 2\sigma(I)$] and wR_2 was 0.0441.

Crystal data for **14**. $C_{67}H_{22}BrF_{32}Hg_4N$ (M = 2331.12 g mol^{-1}), orthorhombic, space group *Pccn*, a = 23.6319(8), b = 12.2246(4) and c = 21.7567(8) Å, V = 6285.3(4) Å^3, Z = 4, T = 120 K, μ(MoK$_\alpha$) = 10.517 mm^{-1}, d_{calc} = 2.463 g cm^{-3}, 69967 reflections measured (3.45° ⩽ 2θ ⩽ 56.00°), 7593 unique (R_{int} = 0.0987, R_{sigma} = 0.0488) which were used in all calculations. The final R_1 was 0.0333 [$I > 2\sigma(I)$] and wR_2 was 0.0642.

CCDC 2166087 and 2309692 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre *via* http://www.ccdc.cam.ac.uk.



Scheme 3

(*av*. 2.96 Å).[9] In the previously described 1 : 1 complex of bromide anion with *o*-carboranylmercury anticrown **7**, also containing four Hg atoms in the cycle, the Hg–Br distances were 3.028(5)–3.087(5) Å (*av*. 3.063 Å).[19] The bromide anion in that adduct deviated from the plane formed by the mercury centres at distances of 0.933–0.999 Å and was also bound to all of them. The Hg–Br separations in the double-decker sandwich complexes of bromide anion with three-mercury macrocycles **3** and **6** were in the ranges of 3.1224(9)–3.3226(9) Å (*av*. 3.22 Å)[8] and 3.132(1)–3.309(1) Å (*av*. 3.21 Å),[20] respectively, and in the bipyramidal dibromide complex of macrocycle **4** they were 3.229(3)–3.453(3) Å (*av*. 3.34 Å).[21]

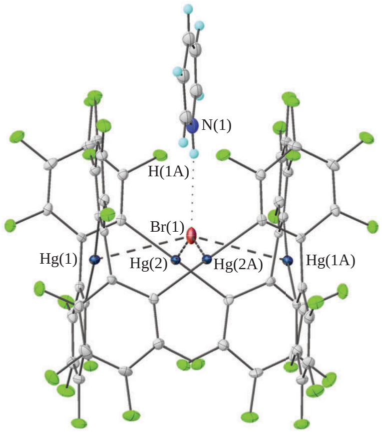


Figure 2 ORTEP representation of the molecular structure of complex **14** in the crystal of **14**·2(PhCH$_3$) with thermal ellipsoids drawn at the 30% probability level. The hydrogen atoms of the C–H bonds of the pyridinium ion, as well as the solvate molecules of toluene, are omitted for clarity. Selected bond lengths (Å) and angles (°): Hg(1)–Br(1) 3.1276(4), Hg(2)–Br(1) 3.3191(4), Hg(1)···Hg(2) 4.7951(4), Hg(1)···Hg(2A) 4.0605(6); Hg(1)–Br(1)–Hg(1A) 152.75(5), Hg(1)–Br(1)–Hg(2) 96.07(1), Hg(1)–Br(1)–Hg(2A) 78.02(1), Hg(2)–Br(1)–Hg(2A) 154.99(5), Hg(2)···Hg(1)···Hg(2A) 93.71(1), Hg(1)···Hg(2)···Hg(1A) 86.29(1). Symmetry transformation used to generate equivalent atoms: –*x* + 3/2, –*y* + 3/2, *z*.

In the crystal, complex **14** occupies a special position on the two-fold rotation axis passing through the bromide ion and perpendicular to the Hg$_4$ plane. Four Hg atoms lie in a plane (maximum deviation from the mean plane is 0.009 Å) resulting in a slightly distorted rectangle, similarly to chloride complex **10**, and in contrast to structures of **1** in its neutral adducts with acetonitrile and water/acetone where Hg atoms form a nearly perfect parallelograms.[9] The Hg–C bond lengths in **14** [2.066(7)–2.074(7) Å] are unexceptional. The C–Hg–C bond angles, as in free **1**, are close to 180° [175.3(3) and 176.0(3)°]. It is interesting that in **10** these C–Hg–C bond angles deviate markedly from 180° and span the range from 166.1(2) to 169.2(2)° [*av*. 167.1(2)°] possibly due to slightly smaller size of chloride anion compared to the macrocycle **1** cavity.

Molecules of complex **14** form a chain along the *c* axis of the crystal, such that the hydrocarbon part of pyridinium ion cycle penetrates into the cavity of the next macrocycle molecule (see Online Supplementary Materials, Figure S2). As a result, the size of the cavities above and below the Hg$_4$ mean plane is virtually the same. This can be characterized by approximately equal distances between the centroids of the phenylene rings in the upper and lower belts of the macrocycle molecule (6.04 and 6.05 Å above plane, 6.08 and 6.14 Å below plane).

In summary, it was shown that the alkenyl bromide complex of hafnocene **12** reacts with cyclic tetrameric perfluoro-*o*,*o*′-biphenylenemercury **1** with the formation of new bromide complex **14** containing pyridinium as the counter cation. As expected, anticrown **1** binds anion very strongly and encapsulates it in its macrocyclic cavity, which leads to the instability and decomposition of the expected electron-deficient hafnium fragment.

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Online Supplementary Materials

Supplementary data associated with this article can be found in the online version at doi: 10.1016/j.mencom.2024.02.009.

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