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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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Table S1. Crystal data and structure refinement parameters for **12**.

Empirical formula	$C_{22}H_{29}BrHf$
Formula weight	551.85
Temperature/K	120
Crystal system	triclinic
Space group	*P*-1
a (Å)	11.2818(4)
b (Å)	13.8692(5)
c (Å)	14.3460(5)
α (deg)	95.2940(10)
β (deg)	104.2230(10)
γ (deg)	104.7640(10)
V (Å^3)	2075.14(13)
Z	4
ρ_{calc}g/cm^3	1.766
μ/mm^{-1}	6.953
F(000)	1072.0
Crystal size/mm^3	0.23 × 0.18 × 0.1
Radiation	MoKα (λ = 0.71073)
$2\theta_{max}$ (deg)	2.97 to 61.448
Index ranges	$-16 \le h \le 16$, $-19 \le k \le 18$, $-20 \le l \le 20$
Reflections collected	28128
Independent reflections	12763 [R_{int} = 0.0227, R_{sigma} = 0.0324]
Data/restraints/parameters	12763/0/445
Goodness-of-fit on F^2	1.018
Final R indexes ($I>=2\sigma (I)$)	R_1 = 0.0224, wR_2 = 0.0441
Final R indexes [all data]	R_1 = 0.0293, wR_2 = 0.0458
Largest diff. peak/hole / e Å^{-3}	0.86/–0.95

Table S2. Crystal data and structure refinement parameters for **14**.

Empirical formula	$C_{67}H_{22}BrF_{32}Hg_4N$
Formula weight	2331.12
Temperature/K	120
Crystal system	orthorhombic
Space group	*P*ccn
a (Å)	23.6319(8)
b (Å)	12.2246(4)
c (Å)	21.7567(8)
α (deg)	90
β (deg)	90
γ (deg)	90
V (Å^3)	6285.3(4)
Z	4
ρ_{calc}g/cm^3	2.463
μ/mm^{-1}	10.517
F(000)	4296
Crystal size/mm^3	0.32 × 0.12 × 0.10
Radiation	MoKα (λ = 0.71073)
$2\theta_{max}$ (deg)	3.45 to 56.00
Index ranges	$-31 \leq h \leq 31$, $-16 \leq k \leq 16$, $-28 \leq l \leq 28$
Reflections collected	69967
Independent reflections	7593 [R_{int} = 0.0987, R_{sigma} = 0.0488]
Data/restraints/parameters	7593/0/473
Goodness-of-fit on F^2	1.037
Final R indexes ($I>=2\sigma(I)$)	R_1 = 0.0333, wR_2 = 0.0642
Final R indexes [all data]	R_1 = 0.0763, wR_2 = 0.0825
Largest diff. peak/hole / e Å^{-3}	2.051/–0.926

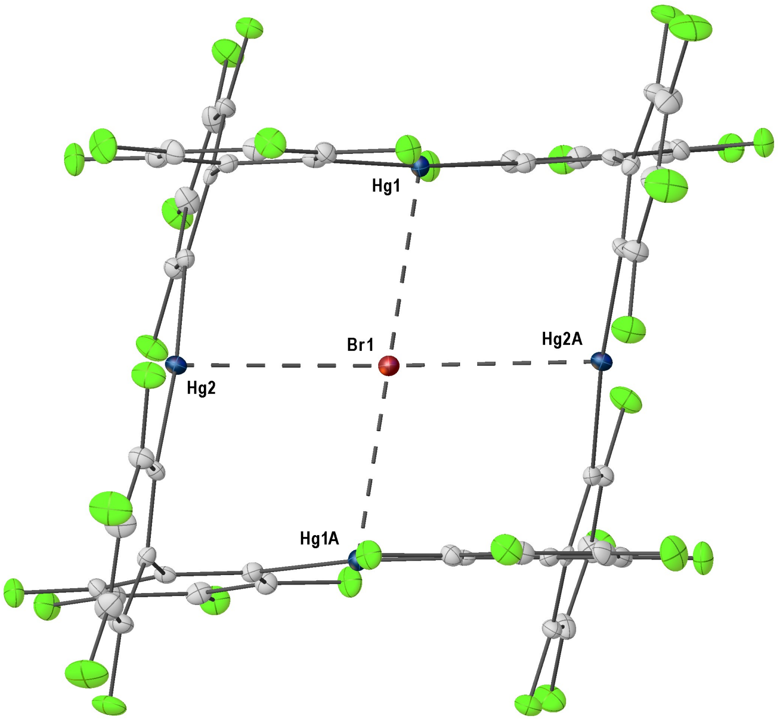

Figure S1. ORTEP representation of the anionic part of complex **14** perpendicular the *c* axis of the crystal with thermal ellipsoids drawn at the 30% probability level.

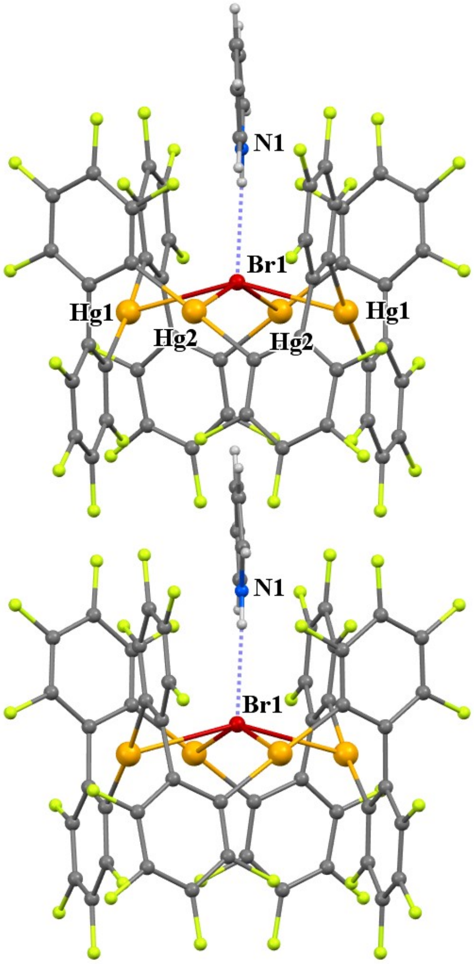

Figure S2. Fragment of a chain of molecules **14** along the *c* axis of the crystal. The pyridinium is disordered over two positions (occupancy 0.5 : 0.5) around the two-fold axis; the bromide anion is disordered over two positions (occupancy 0.95 : 0.05) above and below Hg_4 mean plane (the only position is depicted).

EXPERIMENTAL SECTION

Experiments were carried out under Ar with careful exclusion of air and moisture using standard Schlenk techniques. The starting five-membered hafnacyclocumulene **11** were prepared according to the published procedure.[S1] Commercial $Bu^tC{\equiv}C{-}C{\equiv}CBu^t$ and aniline hydrobromide were purchased from Sigma Aldrich and used without additional purification. Cyclic tetrameric perfluoro-*o*,*o′*-biphenylenemercury **1** was synthesised according the published procedure.[S2] Solvents (pyridine, *n*-hexane) were purified by conventional methods and freshly distilled prior to use over metallic sodium under Ar. The ^1H, ^{13}C and ^{19}F NMR spectra were recorded on a Bruker Av-400 spectrometer. Chemical shifts (^1H, ^{13}C) are given relative to $SiMe_4$ and are referenced to signals of benzene-d$_6$ (δ_H 7.16 ppm, δ_C 128.0 ppm as solvent), the ^{19}F chemical shifts are given relative to $CFCl_3$ as an external standard. The Raman spectra were registered on a JY LABRAM 300 spectrometer (He−Ne laser, 632.8 nm, 5 mW). The mass spectra were recorded on a Finnigan Polaris Q instrument.

Protolysis of complex 11 and synthesis of 12: Complex **11** (0.753 g, 1.60 mmol) was dissolved in pyridine (10 ml) at room temperature, and $PhNH_3Br$ (0.278 g, 1.60 mmol) was added to the resulting light-yellow solution. The next day, the obtained yellow solution was evaporated *in vacuo* to dryness, and the residue was extracted with *n*-hexane (20 ml). The resulted solution was filtered and evaporated to 2-3 ml. The formed crystals were separated, washed with cold *n*-hexane and dried in vacuo. Yield of **12**: 0.547 g (62%). M.p. 122-123°C (under Ar). Anal. calcd. for $C_{22}H_{29}BrHf$: C, 47.88; H, 5.30; Br, 14.48; found C, 47.90; H, 5.34; Br, 14.42. ^1H NMR (C_6D_6, δ, ppm): 1.22 (s, 9H, CMe_3); 1.23 (s, 9H, CMe_3); 6.18 (s, 10H, Cp); 6.69 (s, 1H, C=CH). ^{13}C NMR (C_6D_6, δ, ppm): 28.4 ($\underline{C}Me_3$); 31.3 ($C\underline{Me}_3$); 32.3 ($C\underline{Me}_3$); 42.4 ($\underline{C}Me_3$); 83.6, 100.4 (C≡C); 113.0 (Cp); 113.6 (C=$\underline{C}$H); 215.8 (Zr$\underline{C}$). Raman spectrum (*v*, cm^{-1}): 1523 (C=C), 2201 (C≡C). MS (70 eV, *m/z*): 495 $[M\text{-}{}^t\!Bu]^+$; 389 $[Cp_2HfBr]^+$.

Reaction of 1 with complex 12 and synthesis of 14: Complex **12** (0.076 g, 0.138 mmol) was dissolved in pyridine (2 ml) at room temperature, and compound **1** (0.273 g, 0.137 mmol) was added. The obtained solution was heated at 60°C for 30 h. The resulting brown solution was concentrated by an Ar stream to ~ 0.5 ml. The next day, the formed colourless crystals were separated by decanting of the mother liquor and dried in an argon stream. Yield of **14**: 0.146 g (55%). Anal. calcd. for $C_{53}H_6BrF_{32}Hg_4N$: C, 29.65; H, 0.28; F, 28.32; found C, 29.71; H, 0.43; F, 28.43. ^{19}F NMR (acetone-D_6, δ, ppm): –122.2 (dd, 8F); –138.4 (m, 8F); –154.7 (dd, 8F); –157.2 (m, 8F). The crystals of **14** were grown from pyridine : toluene mixture (2 :1) and not dried in vacuum.

In the another experiment, compound **14** was obtained directly: to a solution of anticrown **1** (0.1703 g, 0.0857 mmol) in acetone - ethanol (1:1, 15 ml) mixture a solution of pyridinium bromide (0.0137 g, 0.0856 mmol) in ethanol (2 ml) was added. The next day, the resulting solution was slowly concentrated to 1 ml at 20°C and the precipitated colourless **14** was filtered off, washed with cold methanol (3 × 0.5 ml, 0°C) and dried in vacuum for 3 h. Yield: 0.0508 g (18%). Anal. calcd. for $C_{53}H_6BrF_{32}Hg_4N$: C, 29.65; H, 0.28; F, 28.32; found C, 29.24; H, 0.41; F, 28.67. ^{19}F NMR (acetone-D_6, δ, ppm): –122.3 (dd, 8F); –138.5 (m, 8F); –154.7 (m, 8F); –157.2 (m, 8F).

X-ray Diffraction Study. Diffraction data for **12** and **14** were collected on a Bruker Kappa APEX II Duo diffractometer using graphite-monochromated Mo-Kα radiation. Semiempirical absorption correction based on equivalent reflections was applied using the SADABS program.[S3] The structures were solved by direct methods and refined by full-matrix least-squares procedures on F^2 with the SHELXTL software package.[S4, S5] Molecular graphics were drawn using the OLEX2/Linux-amd64 program.[S6]

References

S1 V. V. Burlakov, T. Beweries, V. S. Bogdanov, P. Arhdt, W. Baumann, P. V. Petrovskii, A. Spannenberg, K. A. Lyssenko, V. B. Shur and U. Rosenthal, *Organometallics*, 2009, **28**, 2864.

S2 K. I. Tugashov, D. A. Gribanyov, F. M. Dolgushin, A. F. Smol'yakov, A. S. Peregudov, Z. S. Klemenkova, O. V. Matvienko, I. A. Tikhonova and V. B. Shur, *Organometallics*, 2017, **36**, 2437.

S3 *SADABS, Version 2016/5*, Bruker AXS, Madison, Wisconsin, USA.

S4 G. M. Sheldrick, *Acta Crystallogr.,* 2008, **A64**, 112.

S5 G. M. Sheldrick, *Acta Crystallogr*., 2015, **C71**, 3.

S6 O. V. Dolomanov, L. J. Bourhis, R. J. Gildea, J. A. K. Howard and H. Puschmann, *J. Appl. Crystallogr*., 2009, **42**, 339.

NMR spectra of complexes 12 and 14

Figure S3. ^{1}H NMR of **12** (400 MHz, C_6D_6).

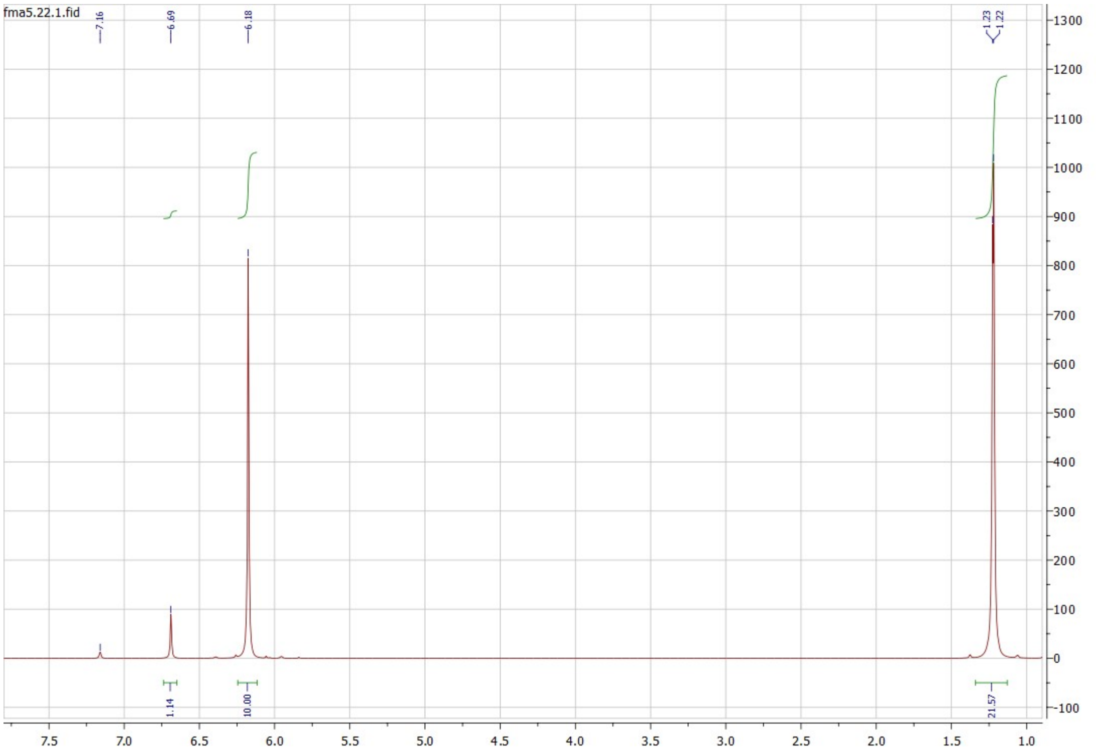

Figure S4. ^{13}C NMR of **12** (400 MHz, C_6D_6).

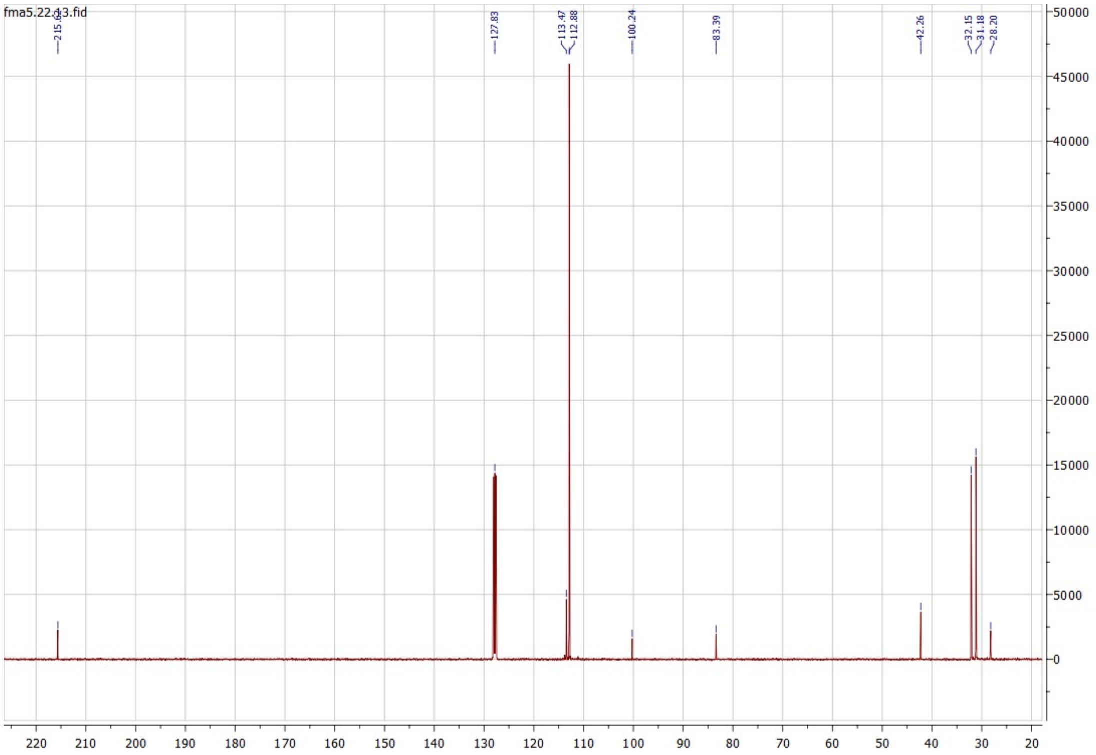

Figure S5. ^{19}F NMR of **14** (acetone-D$_6$).

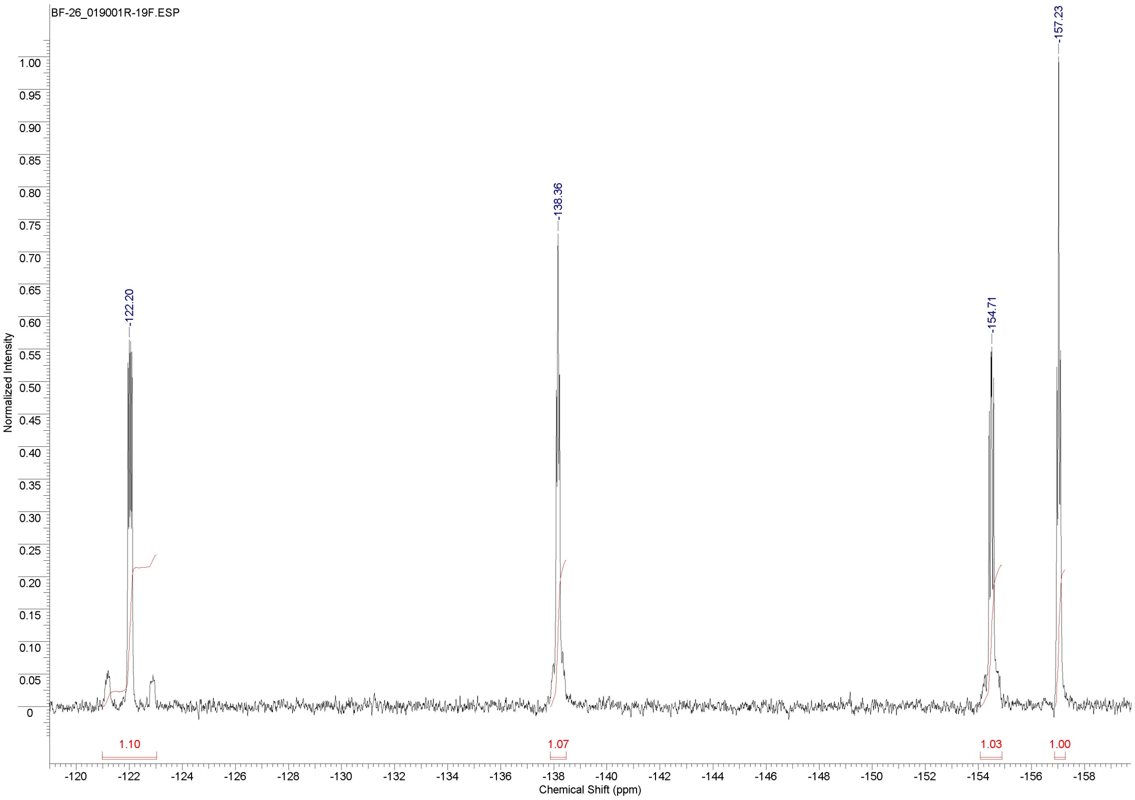

Figure S6. ^{1}H NMR of reaction mixture **12** with **1** (pyridine-D$_5$).

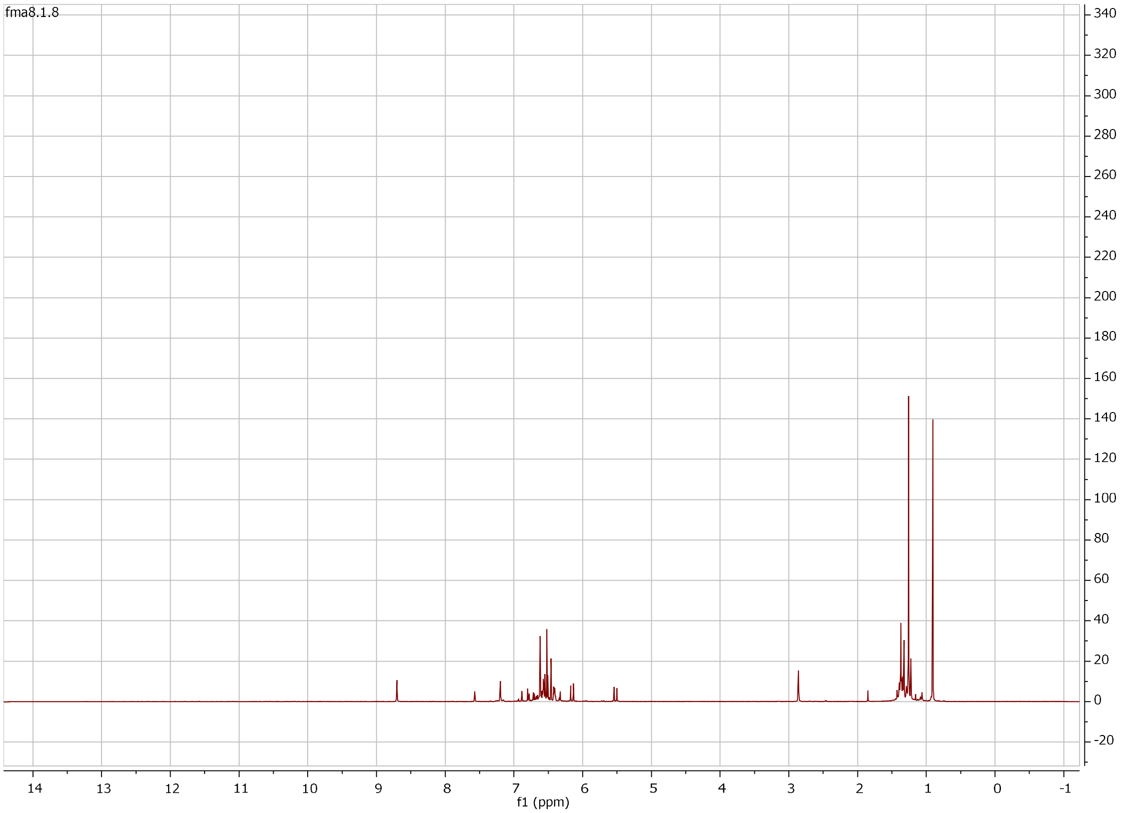

Figure S7. ^{19}F NMR of the reaction mixture between **12** and **1** after 4 hours (pyridine-D$_5$). Signals at –120.6, –137.6, –153.2, –156.3 ppm belong to bromide complex of anticrown **1**; signals at δ –118.2, –136.6, –152.8, –154.0 ppm belong to source **1**.