Electronic supplementary information

η^5-FLUORENYL RHODIUM COMPLEXES: ARE THEY A MYTH OR REALITY?

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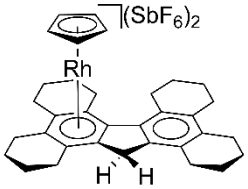
General experimental remarks

All reactions were carried out under an argon atmosphere using distilled solvents. Isolation of the product was carried out in air. $[CpRhI_2]_n$ [1] and hexadecahydrotetrabenzo[*a,c,d,f*]fluorene [2] were synthesized by the previously published procedures. All other reagents were purchased from Acros or Aldrich and used as received. The ^1H and $^{13}C\{^1H\}$ NMR spectra were recorded on a Varian Inova 400 spectrometer operating at 400 and 101 MHz, respectively. The chemical shifts are given in ppm using the residual solvent signals as an internal standard (nitromethane-d_3: 4.42 and 61.35 ppm for ^1H and $^{13}C\{^1H\}$ NMR spectra, respectively).

Preparation of complex 1$(SbF_6)_2$

$MeNO_2$ (1 mL) was added to a mixture of the iodide complex $[CpRhI_2]_n$ (50 mg, 0.118 mmol), hexadecahydrotetrabenzo[*a,c,d,f*]fluorene (54 mg, 0.142 mmol, 1.2 equiv.), and $AgSbF_6$ (81 mg, 0.236 mmol, 2 equiv.). The reaction mixture was vigorously stirred for 2 h, and the precipitate of AgI was centrifuged off. Then, an excess of ether was added. The precipitate that formed was reprecipitated twice from nitromethane by ether. Then the precipitate was washed with cold dichloromethane (2×2 mL) to remove $[Cp_2Rh]SbF_6$. Compound **1**$(SbF_6)_2$ was obtained as a lemon-yellow solid. Yield is 76 mg (63%). Melting point was not measured because decomposition occurs at 89 ºC in air.

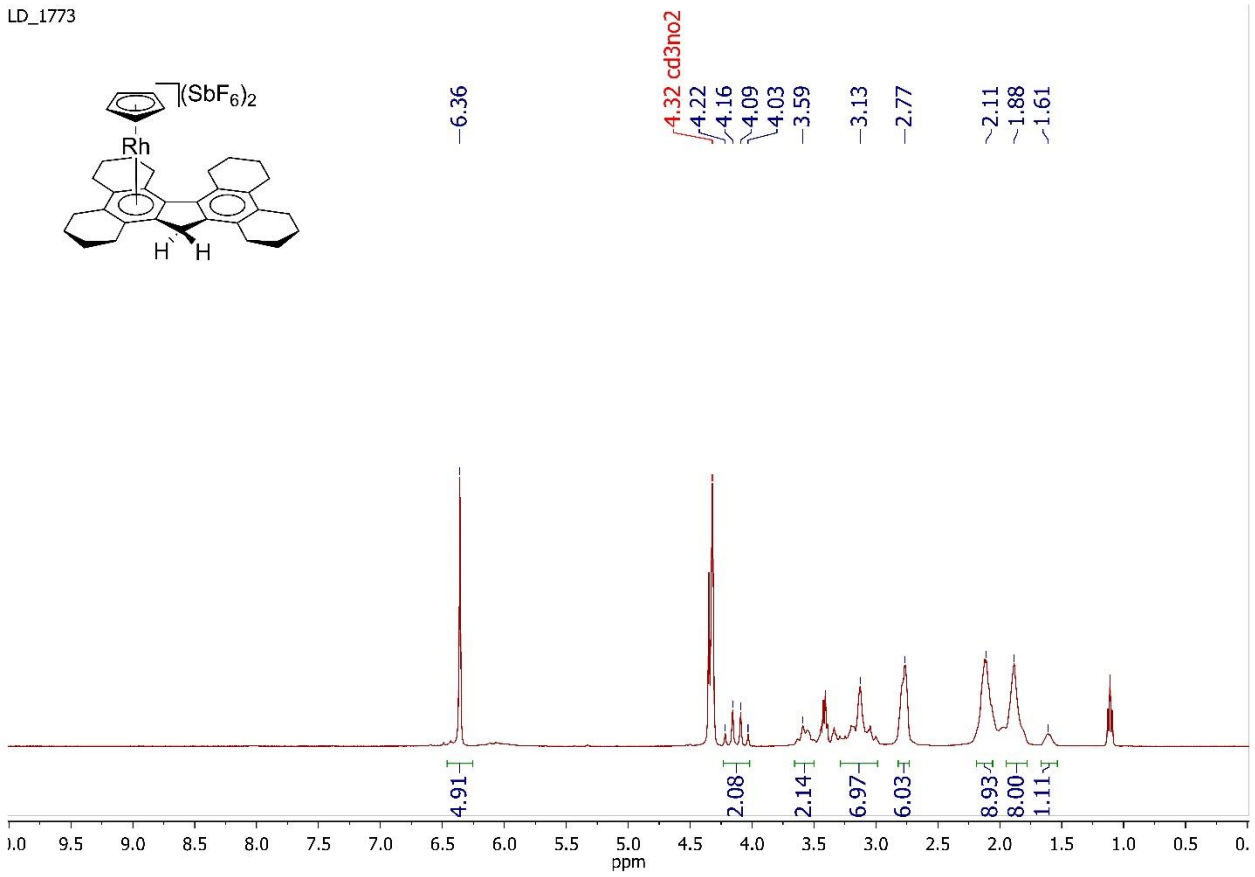
[CpRh(η^6-hexadecahydrotetrabenzo[*a,c,d,f*] fluorene)]$(SbF_6)_2$ (1$(SbF_6)_2$)



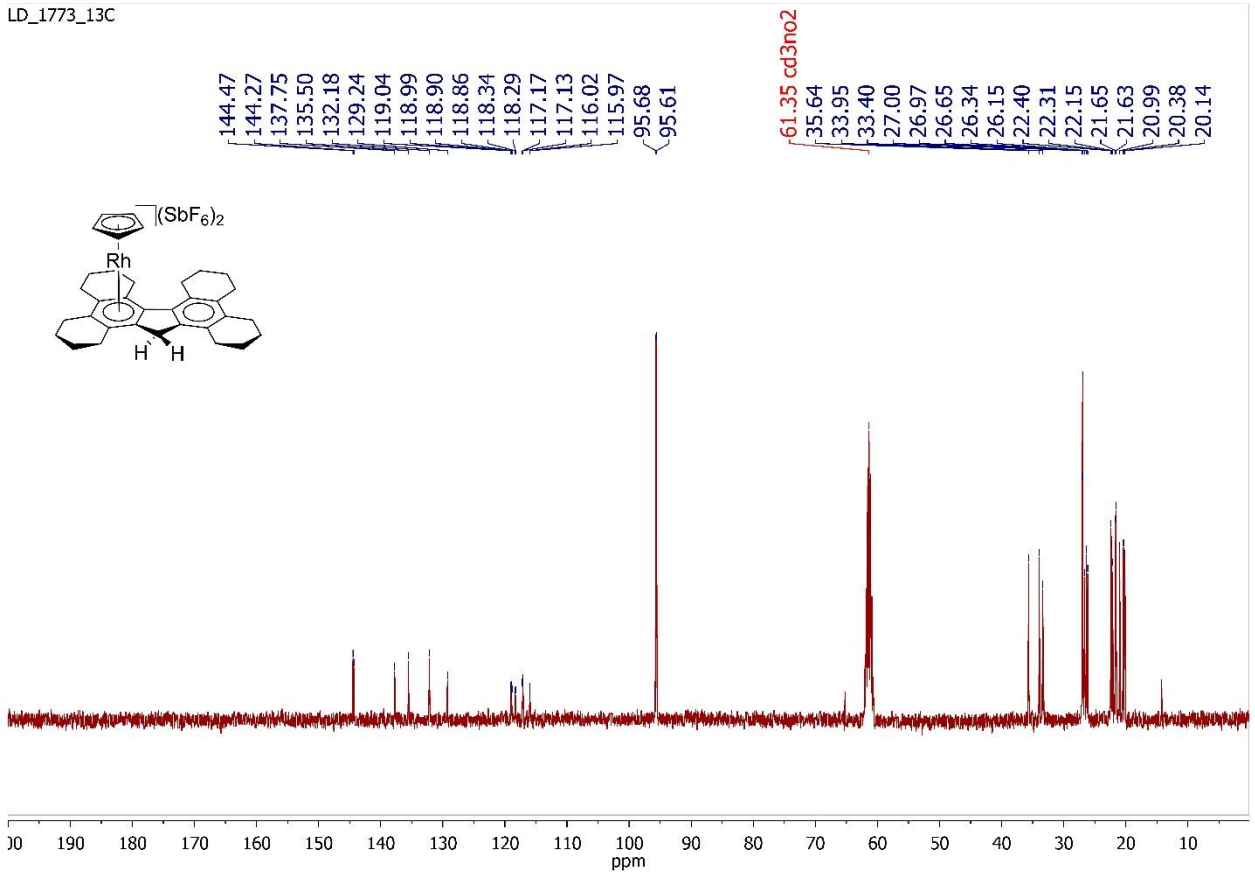
^1H NMR (400 MHz, CD_3NO_2): δ 6.36 (s, 5H), 4.12 (q, J = 23.9 Hz, 2H), 3.66 – 3.50 (m, 2H), 3.29 – 2.99 (m, 7H), 2.82 – 2.73 (m, 6H), 2.19 – 2.06 (m, 9H), 1.95 – 1.78 (m, 8H), 1.66 – 1.54 (m, 1H).
$^{13}C\{^1H\}$ NMR (101 MHz, CD_3NO_2) δ 144.5, 144.3, 137.7, 135.5, 132.2, 129.2, 119.0 (d, J = 5.3 Hz), 118.9 (d, J = 4.4 Hz), 118.3 (d, J = 4.3 Hz), 117.2 (d, J = 4.7 Hz), 116.0 (d, J = 4.5 Hz), 95.6 (d, J = 7.2 Hz), 35.6, 33.9, 33.4, 27.0, 27.0, 26.7, 26.3, 26.1, 22.4, 22.3, 22.2, 21.7, 21.6, 21.0, 20.4, 20.1. Anal. Calcd for $C_{34}H_{39}F_{12}RhSb_2$: C, 39.95; H, 3.85. Found: C, 39.86; H, 3.99%.

NMR spectra

^{1}H NMR (400 MHz) spectrum of 1(SbF$_6$)$_2$ in CD$_3$NO$_2$



^{13}C{^{1}H} NMR (101 MHz) spectrum of 1(SbF$_6$)$_2$ in CD$_3$NO$_2$



Computational details

All calculations were performed using Gaussian 09 software (revision D.01) [3] at the M06L(D3)/LANL2DZ level [4, 5] with corrections for solvation in methanol (the CPCM model implemented in the Gaussian 09 program). Geometry optimizations were performed with convergence options SCF=Tight and Grid=FineGrid.

To estimate the stability of the fluorenyl complexes, we calculated total free energies (ΔG_r) at the temperature of 298.150 K and the pressure of 1.00000 Atm for the reaction of $[CpRh(\eta^5\text{-fluorenyl})]^+$ complex with two water molecules. Similar reactions were calculated for complexes $[Cp_2Rh]^+$ and $[CpRh(\eta^5\text{-indenyl})]^+$ for comparison (Table S1). It was found that only for the fluorenyl derivative the $\eta^5 \rightarrow \eta^1$ rearrangement is exergonic.

Table S1. Sums of electronic and thermal free energies for the starting compounds (E_{SC}) and the adducts with two water molecules (E_{AW}), as well as total free energies (ΔG_r) for the reaction of rhodium complexes with water

Ligand	E_{SC} (in hartree)	E_{AW} (in hartree)	ΔG_r (in kcal·mol^{-1})
Cyclopentadienyl	–649.036876	–648.996058	–25.6
Indenyl	–802.590384	–802.569280	–13.24
Fluorenyl	–956.145740	–956.148263	1.58

$[CpRh(\eta^5\text{-cyclopentadienyl})]^+ \cdot 2H_2O$

45	-0.014043000	0.217619000	-0.300960000
6	0.682916000	1.713718000	1.201935000
6	-0.755108000	1.616913000	1.270519000
6	-1.290933000	2.024537000	-0.006290000
6	-0.183999000	2.372931000	-0.864189000
1	-0.254893000	2.714916000	-1.882732000
6	1.035971000	2.179779000	-0.117701000
6	-1.110189000	-1.496471000	-1.204424000
1	-2.148047000	-1.448591000	-1.489744000
6	-0.606770000	-1.893212000	0.090240000
1	-1.229150000	-2.146242000	0.935401000
6	0.833689000	-1.811055000	0.051876000
1	1.523364000	-1.990061000	0.863539000
6	1.218519000	-1.363426000	-1.267235000
1	2.227461000	-1.196701000	-1.607016000
6	0.017455000	-1.168524000	-2.044543000
1	-0.028448000	-0.838436000	-3.068495000
8	3.371272000	-1.161376000	1.671643000
1	3.629282000	-0.413098000	1.102975000
1	4.119246000	-1.373188000	2.259084000
8	-3.195871000	-1.455679000	1.691732000
1	-3.897369000	-1.710190000	2.318449000
1	-3.506347000	-0.687060000	1.179044000
1	2.034785000	2.350809000	-0.482224000
1	1.371655000	1.476426000	1.995424000
1	-1.328206000	1.296076000	2.124036000
1	-2.333899000	2.057796000	-0.272660000

$[CpRh(\eta^1\text{-cyclopentadienyl})(H_2O)_2]^+$

45	-0.455813000	0.191450000	0.037913000
6	2.968379000	-1.130367000	0.495426000
6	3.367409000	0.138105000	-0.112223000

6	2.421628000	0.497842000	-1.053999000
6	1.354221000	-0.510626000	-1.056885000
1	0.863897000	-0.778112000	-1.990563000
6	1.788650000	-1.546351000	-0.100555000
6	-2.154219000	-0.146217000	-1.278643000
1	-2.215886000	0.208162000	-2.293543000
6	-2.711643000	0.524990000	-0.099251000
1	-3.173754000	1.498773000	-0.099662000
6	-2.469619000	-0.284704000	1.034523000
1	-2.710894000	-0.043979000	2.056053000
6	-1.738791000	-1.471040000	0.590282000
1	-1.410637000	-2.281790000	1.219492000
6	-1.631614000	-1.418485000	-0.849095000
1	-1.172828000	-2.164479000	-1.476761000
8	0.247062000	2.268098000	-0.178528000
1	1.103495000	2.397877000	-0.630665000
1	-0.382059000	2.973751000	-0.414544000
8	0.791866000	0.515384000	1.813253000
1	1.644911000	0.020580000	1.770684000
1	0.953823000	1.474816000	1.913809000
1	4.267158000	0.685759000	0.132747000
1	2.487206000	1.334397000	-1.738776000
1	3.526025000	-1.662145000	1.254186000
1	1.253275000	-2.465586000	0.096174000

$[CpRh(\eta^5\text{-indenyl})]^+ \cdot 2H_2O$

45	-0.524394000	-0.078024000	-0.381950000
6	-0.096587000	-1.826211000	0.912218000
6	1.196439000	-1.190793000	0.727451000
6	2.117471000	-0.609518000	1.641646000
1	1.906824000	-0.605963000	2.703279000
6	3.293736000	-0.073787000	1.139283000
1	4.020205000	0.352526000	1.819735000
6	3.581053000	-0.075324000	-0.263811000
1	4.514983000	0.352807000	-0.604919000
6	2.698459000	-0.617967000	-1.184316000
1	2.923981000	-0.621870000	-2.242792000
6	1.491918000	-1.197229000	-0.703384000
6	0.380552000	-1.842090000	-1.379752000
1	0.306594000	-2.025246000	-2.439019000
6	-0.553764000	-2.287744000	-0.375547000
6	-0.637279000	2.044449000	-1.102158000
1	0.200733000	2.565525000	-1.535405000
6	-0.972860000	2.010210000	0.310814000
1	-0.395290000	2.491643000	1.085670000
6	-2.146678000	1.201303000	0.471069000
1	-2.638999000	0.923265000	1.391313000
6	-2.526202000	0.712901000	-0.840837000
1	-3.363325000	0.068961000	-1.055761000
6	-1.604006000	1.259618000	-1.814982000
1	-1.631520000	1.089390000	-2.877781000
8	-3.575057000	-0.929101000	2.192668000
1	-3.551063000	-1.615651000	1.501187000
1	-4.108822000	-1.262671000	2.936756000
8	1.767460000	2.944953000	1.236254000
1	2.508026000	3.337969000	1.733777000
1	2.082688000	2.120069000	0.819154000

1	-1.459492000	-2.841126000	-0.560814000
1	-0.590517000	-1.992278000	1.855835000

[CpRh(η^1-indenyl)(H_2O)$_2$]$^+$

45	-1.088555000	0.173011000	0.103735000
6	1.906539000	-1.624969000	-0.604970000
1	1.187519000	-2.329934000	-1.009852000
6	3.067589000	-2.091579000	0.038594000
1	3.242304000	-3.157907000	0.121894000
6	4.006279000	-1.189276000	0.579076000
1	4.888422000	-1.572254000	1.078778000
6	3.814687000	0.199487000	0.469207000
1	4.546294000	0.889497000	0.874587000
6	2.665461000	0.672981000	-0.185871000
6	2.215001000	2.026655000	-0.504303000
6	1.021250000	1.947412000	-1.183885000
6	0.576495000	0.543383000	-1.281224000
1	0.114851000	0.215024000	-2.211232000
6	1.699577000	-0.243760000	-0.712314000
6	-2.776119000	-0.370173000	-1.152830000
1	-3.114232000	0.200901000	-2.000886000
6	-3.345520000	-0.314144000	0.200989000
1	-4.092551000	0.390892000	0.528498000
6	-2.687455000	-1.263762000	1.007012000
1	-2.838717000	-1.429100000	2.060394000
6	-1.675261000	-1.923365000	0.178232000
1	-0.999518000	-2.695325000	0.510008000
6	-1.815003000	-1.445391000	-1.175097000
1	-1.253644000	-1.783645000	-2.030038000
8	-1.149619000	2.302292000	0.705162000
1	-0.515009000	2.912523000	0.279834000
1	-2.015476000	2.733832000	0.823276000
8	0.296413000	0.341020000	1.826612000
1	1.257676000	0.234609000	1.668791000
1	0.115642000	1.209378000	2.240406000
1	2.760005000	2.930055000	-0.266285000
1	0.485927000	2.778452000	-1.626146000

[CpRh(η^5-fluorenyl)]$^+$ ·2H_2O

45	-0.000188000	0.526103000	-0.416386000
6	-2.561961000	-1.378805000	-1.291542000
1	-2.893840000	-1.246785000	-2.313354000
6	-3.466020000	-1.593085000	-0.264050000
1	-4.526031000	-1.628174000	-0.480942000
6	-3.031419000	-1.780653000	1.086644000
1	-3.773458000	-1.962134000	1.854182000
6	-1.685764000	-1.749022000	1.428220000
1	-1.368418000	-1.900978000	2.452323000
6	-0.731063000	-1.541369000	0.398742000
6	0.730230000	-1.541459000	0.399331000
6	1.684025000	-1.749284000	1.429596000
1	1.365802000	-1.901055000	2.453452000
6	3.029941000	-1.781318000	1.089103000
1	3.771319000	-1.962877000	1.857260000
6	3.465669000	-1.594015000	-0.261256000
1	4.525845000	-1.629488000	-0.477302000
6	2.562484000	-1.379560000	-1.289510000
1	2.895231000	-1.247751000	-2.311063000

6	1.173452000	-1.361914000	-0.979937000
6	0.000508000	-1.154365000	-1.811605000
1	0.000971000	-1.022753000	-2.881704000
6	-1.173151000	-1.361661000	-0.980874000
6	1.157777000	2.384964000	-0.704110000
1	2.184288000	2.372703000	-1.033364000
6	0.715023000	2.368807000	0.684038000
1	1.381126000	2.315788000	1.531710000
6	-0.709634000	2.368128000	0.689751000
1	-1.369014000	2.314718000	1.542542000
6	-1.163223000	2.383267000	-0.694675000
1	-2.192230000	2.369278000	-1.015950000
6	-0.006149000	2.438906000	-1.553083000
1	-0.010619000	2.476225000	-2.629044000
8	-3.389686000	1.453158000	1.787875000
1	-3.172271000	0.595053000	1.373086000
1	-4.187308000	1.335148000	2.335791000
8	3.397198000	1.453500000	1.779425000
1	4.194237000	1.334101000	2.327882000
1	3.178403000	0.595694000	1.364760000

$[CpRh(\eta^1\text{-fluorenyl})(H_2O)_2]^+$

45	-1.356483000	0.271272000	0.193629000
6	0.501360000	-2.599144000	-0.879713000
1	-0.432216000	-2.784189000	-1.401233000
6	1.244736000	-3.674114000	-0.360673000
1	0.882172000	-4.687428000	-0.487243000
6	2.454642000	-3.448955000	0.326344000
1	3.007468000	-4.290800000	0.726276000
6	2.953547000	-2.145233000	0.490339000
1	3.892765000	-1.979868000	1.007077000
6	2.221925000	-1.070457000	-0.035029000
6	2.504505000	0.366410000	-0.072457000
6	3.596039000	1.110470000	0.393710000
1	4.408739000	0.630725000	0.928306000
6	3.634587000	2.493714000	0.142831000
1	4.473557000	3.081135000	0.496275000
6	2.601516000	3.122422000	-0.579179000
1	2.658000000	4.185286000	-0.781772000
6	1.496583000	2.382061000	-1.043078000
1	0.710593000	2.868272000	-1.613673000
6	1.439647000	1.004005000	-0.776748000
6	0.392014000	0.011600000	-1.107156000
1	-0.085243000	0.092491000	-2.083264000
6	0.984043000	-1.293817000	-0.712594000
6	-3.001698000	0.841023000	-1.109703000
1	-2.966808000	1.658308000	-1.810340000
6	-3.591815000	0.892047000	0.236664000
1	-3.953767000	1.786067000	0.718501000
6	-3.511845000	-0.389836000	0.809899000
1	-3.803962000	-0.667584000	1.808738000
6	-2.855886000	-1.272185000	-0.161060000
1	-2.655944000	-2.321515000	-0.015784000
6	-2.652759000	-0.531098000	-1.380281000
1	-2.244609000	-0.917620000	-2.299419000
8	-0.451620000	2.035787000	1.167240000
1	0.266386000	2.508301000	0.688746000

1	-1.059718000	2.669855000	1.590326000
8	-0.198067000	-0.516576000	1.908440000
1	0.444047000	-1.243748000	1.789768000
1	0.230928000	0.257897000	2.327261000

X-ray diffraction study

Crystals of **1**$(SbF_6)_2$ were grown by slow interdiffusion of a two-phase system containing ether and a solution of the compound in nitromethane. X-ray diffraction data were collected at 120 K with a Bruker APEX2 DUO CCD diffractometer, using graphite monochromated Mo-Kα radiation (λ = 0.71073 Å, ω-scans). Using Olex2 [6], the structure was solved with the ShelXT [7] structure solution program using Intrinsic Phasing and refined with the XL [8] refinement package using Least-Squares minimization against F^2 in the anisotropic approximation for non-hydrogen atoms. Positions of hydrogen atoms were calculated, and they were refined in the isotropic approximation in the riding model. Crystal data and structure refinement parameters are given in Table S2. CCDC 2389361 (**1**$(SbF_6)_2$) contain the supplementary crystallographic information for this paper.

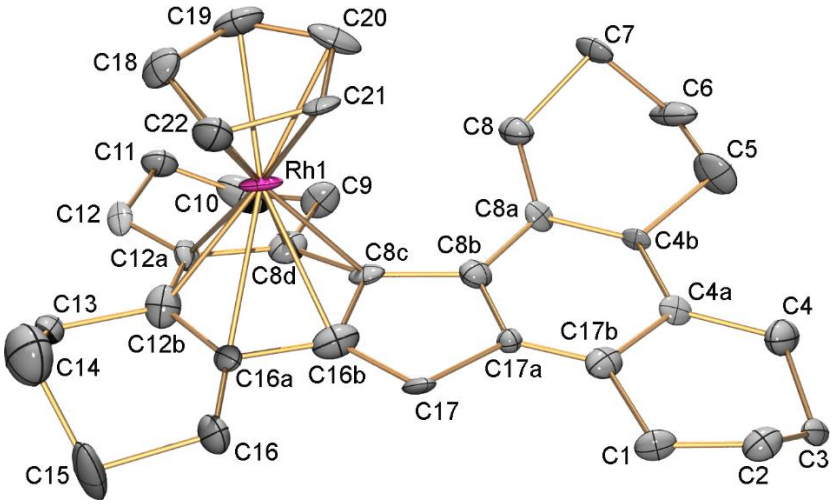


Figure S1. General view of **1**$(SbF_6)_2$ in the representation of atoms as 50% probability ellipsoids; hydrogen atoms are omitted. Bond lengths [Å]: C13 - C14 1.57(3), C14 - C15 1.509(19), C15 - C16 1.67(4),C16 - C16A 1.51(4), C16A - C16B 1.57(3), C16A - Rh1 2.39(3), C16B - C17 1.48(3), C16B - Rh1 2.32(2), C17 - C17A 1.52(3), C17A - C17B 1.21(3), C1 - C2 1.34(4), C1 - C17B 1.53(4), C2 - C3 1.48(2), C18 - C19 1.42(2), C3 - C4 1.40(5), C18 - C22 1.39(2), C4 - C4A 1.60(4), C18 - Rh1 2.08(4), C4A - C4B 1.37(3), C4A - C17B 1.43(3), C19 - C20 1.38(3), C19 - Rh1 2.16(4), C4B - C5 1.65(3), C4B - C8A 1.38(2), C20 - C21 1.45(2), C20 - Rh1 2.18(2),C5 - C6 1.36(3), C6 - C7 1.50(2), C21 - C22 1.46(2), C7 - C8 1.63(4), C21 - Rh1 2.10(3), C8 - C8A 1.56(3), C8A - C8B 1.34(3), C22 - Rh1 1.85(3), C8B - C8C 1.47(2), C8B - C17A 1.35(3), C8C - C8D 1.567(19), C8C - C16B 1.52(3), C8C - Rh1 2.30(2), C8D - C9 1.54(3), C8D - C12A 1.4191, C8D - Rh1 2.2587, C9 - C10 1.46(4), C10 - C11 1.482(17), C11 - C12 1.69(2), C12 - C12A 1.31(3), C12A - C12B 1.50(3), C12A - Rh1 2.3260, C12B - C13 1.44(4), C12B - C16A 1.37(4), C12B - Rh1 2.29(3).

Table S2. Crystal data and structure refinement parameters for complex **1**$(SbF_6)_2$

	1$(SbF_6)_2$
Formula unit	$C_{34}H_{39}F_{11}RhSb_2$
Formula weight	1003.06
Crystal system	Orthorhombic
Space group	$Pca2_1$
Z	4
a, Å	25.243(4)
b, Å	10.3847(14)
c, Å	14.951(2)

α, °	90
β, °	90
γ, °	90
V, Å^3	3919.3(9)
D_{calc} (g cm^{-1})	1.700
Linear absorption, μ (cm^{-1})	18.59
F(000)	1956
$2\Theta_{max}$, °	50
Reflections measured	31902
Independent reflections	6886
Observed reflections [$I > 2\sigma(I)$]	4628
Parameters	425
R1	0.0722
wR2	0.1977
GOOF	1.048
$\Delta\rho_{max}/\Delta\rho_{min}$ (e Å^{-3})	3.052/–2.397

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