Supporting Information

Heterobimetallic 21,23-dimetallaporphyrin: activation of metal-metal interactions within the porphyrinoid macrocycle

Grzegorz Vetter, Agata Białońska, Aneta Jezierska, Jarosław J. Panek and Ewa Pacholska-Dudziak*

Department of Chemistry University of Wroclaw ul. Joliot-Curie 14, 50-383 Wroclaw, Poland

E-mail: ewa.dudziak@uwr.edu.pl

Contents:

1. Materials and methods 3

2. Synthesis and characterization 3

3. Computational methodology 15

3.1. Calculations focused on metal–metal bond analysis 15

3.2. Calculations of possible structures of **4-Rh(CO)$_2$Cl** 15

4. Computational results 15

4.1. Energetic and structural considerations 15

4.2. Metal–metal bonding – QTAIM and ELF description 17

4.3. Natural Bond Orbital (NBO) parameters for the metal–metal bonding 19

4.4. Calculations of possible structures of **4-Rh(CO)$_2$Cl** 20

5. References 30

List of figures and tables:

Figure S1. HRMS ESI (+MS) spectra of **4-Rh(CO)$_2$Cl** 6
Figure S2. ^{1}H NMR spectrum of **4-Rh(CO)$_2$Cl** 6
Figure S3. ^{1}H NMR spectrum of **5** 7
Figure S4. Variable temperature ^{1}H NMR spectra of **5** 8
Figure S5. ^{13}C NMR spectrum of **5** 9
Figure S6. HRMS ESI (+MS) spectra of **5** 10
Figure S7. Variable temperature ^{1}H NMR spectra of **5-Cl$_2$** 11
Figure S8. ^{13}C NMR spectrum of **5-Cl$_2$** 12
Figure S9. HRMS ESI (+MS) spectra of **5-Cl$_2$** 13
Figure S10. Absorption spectrum of **4-Rh(CO)$_2$Cl** 13
Figure S11. X-ray structure of **5** 14
Figure S12. Angles around the central part of **5** 14
Table S1. Energies of the DFT-optimized structures of **1**, **5** and **5-Cl$_2$** and metal–metal distances 16
Figure S13. Topology of electron density in the vicinity of metal centers of **1**, **5** and **5-Cl$_2$** ..17
Table S2. QTAIM parameters of the metal–metal bond critical points 18
Table S3. QTAIM parameters of selected BCPs in **5** 18
Figure S14. Electron Localization Function (ELF) along the metal–metal line in **1**, **5** and **5-Cl$_2$** 19
Table S4. NBO parameters for the metal–metal interactions 20
Figure S15. Energy diagram for conformational interconversions of **5** and **5-Cl$_2$** 20
Figure S16. DFT-optimized possible structures of **4-Rh(CO)$_2$Cl** 21
Table S5. Cartesian coordinates of DFT optimized structures of **5** and **5-Cl$_2$** 21
Table S6. Cartesian coordinates of DFT optimized transition states **[5]**‡ and **[5-Cl$_2$]**‡ 23
Table S7. Cartesian coordinates of DFT optimized geometries of **4-Rh(CO)$_2$Cl** 24

1. Materials and methods

All reagents and solvents were purchased from commercial sources and used without further purification. Dichloromethane was distilled from calcium hydride. Column chromatography was carried out on Macherey-Nagel silica gel 60. NMR spectra were recorded on Bruker Avance III 500 MHz and 600 MHz spectrometers. Chemical shifts were reported in ppm with reference to residual protons and carbons of $CDCl_3$ (δ 7.26 ppm in ^{1}H NMR, δ 77.2 ppm in ^{13}C NMR), CD_2Cl_2 (δ 5.32 ppm in ^{1}H NMR, δ 54.0 ppm in ^{13}C NMR) and toluene-d_8 (δ 2.09 ppm in ^{1}H NMR). UV-Vis spectra were recorded on a Varian Carry 60 spectrophotometer equipped with a Peltier temperature controller and stirrer using 1 cm path length optical glass cuvettes. Mass spectra were carried out on a Bruker Apex-ultra FTMS and Bruker micrOTOF-Q spectrometers using electrospray ionization.

Single-crystal X-ray diffraction data were collected at 100 K, on Xcalibur (Onyx CCD detector) (**5-Cl$_2$**) or XtaLAB Synergy R, DW system (HyPix-Arc 150) (**5**) κ-geometry diffractometers using *Cu* K*α* radiation. Data reduction and analysis were carried out with the CrysAlis Pro programs (CrysAlis PRO. *CrysAlisPro: Rigaku Oxford Diffraction 1.171.41.80a*). The structures were solved by direct methods and refined with the full-matrix least-squares technique using the *SHELXS*[1] and *Shelxl-2018/3*[2] programs. Hydrogen atoms were placed at calculated positions. Before the last cycle of refinement, all H atoms were fixed and were allowed to ride on their parent atoms. Anisotropic displacement parameters were refined for all non-hydrogen atoms. However, SIMU or ISOR restraints were applied in **5** and additionally, EADP constrains in **5-Cl$_2$**. The Rh–C(carbonyl) distance of the disordered components was restrained applying the SADI command. The occupancy factors for the disordered components were refined.

Electrochemical measurements were performed by means of Autolab PGSTAT100N (Metrohm) potentiostat/galvanostat system for dichloromethane solutions with a glassy carbon, a platinum wire, and Au as the working, auxiliary, and reference electrodes, respectively. Tetrabutylammonium hexafluorophosphate ($[Bu_4N]PF_6$) was used as a supporting electrolyte in cyclic voltammetry measurements and tetrabutylammonium perchlorate ($[Bu_4N]ClO_4$) was used in differential pulse voltammetry. The given potentials were referenced with the ferrocene/ferrocenium couple used as an internal standard.

2. Synthesis and characterization

Synthesis of 4:[3] 30 mg of 5,10,15,20-tetrakis(4-methoxyphenyl)-21,23-ditelluraporphyrin, **3**,[4] ($3.1\cdot10^{-5}$ mol) and 22 mg ($4.7\cdot10^{-5}$ mol) of $Pt(PhCN)_2Cl_2$ were dissolved in 15 ml toluene. The nitrogen was bubbled through the mixture for 15 minutes, and the solution was refluxed for another 15 minutes. The solvent was evaporated, and the product was purified by column chromatography on SiO_2, and **4** was eluted as a red band with 1% ethanol in CH_2Cl_2 (14,3 mg, 45%). **^{1}H NMR ($CDCl_3$, 300 K, 500 MHz):** δ 10.75 (d, $^3J_{HH}$ = 4.5 Hz, $^3J_{PtH}$ = 84 Hz, 1H,

platinacycle), 10.26 (d, $^3J_{HH}$ = 4.5 Hz, $^3J_{PtH}$ = 98 Hz, 1H, platinacycle), 9.99 (d, $^3J_{HH}$ = 6.8 Hz, 1H, tell), 9.90 (d, $^3J_{HH}$ = 6.8 Hz, 1H, tell), 8.62 (AB, $^3J_{HH}$ = 4.8 Hz, 2H, pyrr), 8.37 (d, $^3J_{HH}$ = 4.4 Hz, 1H, pyrr), 8.20 (m, 2H, *o*-Ph), 8.14 (d, $^3J_{HH}$ = 4.4 Hz, 1H, pyrr), 8.11 (m, 2H, *o*-Ph), 8.07 (m, 2H, *o*-Ph), 8.00 (m, 2H, *o*-Ph), 7.38 (m, 2H, *m*-Ph), 7.31 (m, 4H, *m*-Ph), 7.27 (m, 2H, *m*-Ph), 4.10 (s, 3H, OMe), 4.09 (s, 3H, OMe), 4.06 (s, 3H, OMe), 4.03 (s, 3H, OMe); **UV-Vis (nm):** 864, 791, 724, 526, 481, 374, 317; **HRMS (ESI)** *m/z* = 1030.1474, calc. for $C_{48}H_{36}N_2O_4{}^{130}Te^{195}Pt$, $[M+H]^+$: 1030.1469.

Synthesis of 4-Rh(CO)$_2$Cl: Solution of 21-platina-23-telluraporphyrin **4** (10 mg, $9.7\cdot10^{-6}$ mol) and $[Rh(CO)_2Cl]_2$ (3.8 mg, $9.7\cdot10^{-6}$ mol) in $CDCl_3$ (0.6 ml) was shaken in NMR tube for five minutes. Formation of **4-Rh(CO)$_2$Cl** was observed in the ^{1}H NMR spectrum. At room temperature **4-Rh(CO)$_2$Cl** converted in the $CDCl_3$ solution to a mixture of products, including **5**, in several days. **^{1}H NMR ($CDCl_3$, 280 K, 600 MHz):** δ 10.43 (d, $^3J_{HH}$ = 4.5 Hz, 1H, platinacycle), 9.94 (d, $^3J_{HH}$ = 4.5 Hz, 1H, platinacycle), 9.66 (AB, 2H, tell), 8.91 (d, $^3J_{HH}$ = 4.9 Hz, 1H, pyrr), 8.67 (d, $^3J_{HH}$ = 4.9 Hz, 1H, pyrr), 8.62 (m, 1H, *o*-Anis), 8.40 (m, 2H, *o*-Anis), 8.26 (d, $^3J_{HH}$ = 4.5 Hz, 1H, pyrr), 8.17 (m, 2H, *o*-Anis), 8.09 (m, 2H, *o*-Anis), 7.92 (d, $^3J_{HH}$ = 4.5 Hz, 1H, pyrr), 7.79 (m, 1H, *o*-Anis), 7.46 (m, 2H, *m*-Anis), 7.45 (m, 1H, *m*-Anis), 7.36 (m, 4H, *m*-Anis), 7.21 (m, 1H, *m*-Anis), 4.12 (s, 3H, OMe), 4.09 (s, 3H, OMe), 4.07 (s, 3H, OMe), 4.05 (s, 3H, OMe); **^{13}C NMR ($CDCl_3$, 280 K, 150 MHz):** δ 184.1 (α-platinacycle), 178.2 (d, $^1J_{RhCO}$ = 77 Hz, CO), 174.7 (α-pyrr), 171.3 (β-platinacycle), 165.6 (α-pyrr), 163.4 (α-pyrr), 161.8 (para), 160.8 (para), 160.5 (para), 160.4 (para), 157.0 (α-platinacycle), 152.4 (meso), 151.4 (α-tell), 149.7 (α-tell), 148.1 (β-tell), 147.2 (β-platinacycle), 146.6 (α-pyrr), 144.3 (meso), 143.0 (meso), 142.4 (β-pyrr), 139.6 (β-tell, meso), 138.5 (*o*-Anis), 137.1 (*o*-Anis), 136.7 (*o*-Anis), 136.3 (ipso), 136.0 (*o*-Anis), 135.9 (ipso), 134.1 (*o*-Anis), 131.4 (ipso), 130.9 (β-pyrr), 129.0 (β-pyrr), 128.5 (β-pyrr), 128.3 (ipso), 115.3 (*m*-Anis), 114.8 (*m*-Anis), 113.4 (*m*-Anis), 56.0 (OMe), 55.9 (OMe), 55.8 (OMe); **UV-Vis,** nm: 480 (sh), 540 (sh), 725 (sh), 873, 955; **HRMS (ESI)** *m/z* = 1188.0283, calc. for $C_{48}H_{36}N_2O_4{}^{130}Te^{195}PtRh(CO)_2$, $[M-Cl]^+$: 1188.0345.

Synthesis of 5: 20 mg ($1.9\cdot10^{-5}$ mol) of 21-platina-23-telluraporphyrin **4** and 7.6 mg ($1.9\cdot10^{-5}$ mol) of $[Rh(CO)_2Cl]_2$ were dissolved in 15 ml of toluene. Nitrogen was bubbled through the mixture for 15 minutes and the solution was stirred for 5 days at room temperature. After evaporation of the solvent, the product was purified by column chromatography on SiO_2, and product **5** was eluted with CH_2Cl_2 as a red band (8.1 mg, 40%). **^{1}H NMR (CD_2Cl_2, <u>300 K</u>, 600 MHz):** δ 10.07 (bd, 1H, rhodacycle), 9.90 (bd, 1H, platinacycle), 9.61 (bd, 1H, platinacycle), 9.45 (bd, 1H, rhodacycle), 8.65 (bd, 1H, pyrr), 8.58 (bd, 1H, pyrr), 8.42 (bd, 1H, pyrr), 8.32 (bd, 1H, pyrr), 8.22–8.08 (m, 8H, *o*-Anis), 7.38–7.28 (m, 8H, *m*-Anis), 4.08 (bs, 6H, OMe), 4.05 (s, 3H, OMe), 4.01 (s, 3H, OMe); **^{1}H NMR (CD_2Cl_2, <u>220 K</u>, 600 MHz):** δ 10.12 (dd, $^3J_{HH}$ = 5.3 Hz, $^3J_{RhH}$ = 1.5 Hz, 1H, rhodacycle), 9.92 (d, $^3J_{HH}$ = 4.2 Hz, 1H, platinacycle), 9.65 (d, $^3J_{HH}$ = 4.2 Hz, 1H, platinacycle), 9.52 (dd, $^3J_{HH}$ = 5.3 Hz, $^3J_{RhH}$ = 1.5 Hz, 1H, rhodacycle), 8.63 (AB, 2H, pyrr), 8.51 (m, 1H, *o*-Anis), 8.42 (d, $^3J_{HH}$ = 4.5 Hz, 1H, pyrr), 8.41 (m, 1H, *o*-Anis), 8.26 (d, $^3J_{HH}$ = 4.6 Hz, 1H, pyrr), 8.23 (m, 2H, *o*-Anis), 8.05 (m, 2H, *o*-Anis), 7.73 (m, 1H, *o*-

Anis), 7.58 (m, 1H, *o*-Anis), 7.41 (m, 1H, *m*-Anis), 7.36 (m, 2H, *m*-Anis), 7.34 (m, 1H, *m*-Anis), 7.23 (m, 3H, *m*-Anis), 7.17 (m, 1H, *m*-Anis), 4.03 (s, 3H, OMe), 4.01 (s, 3H, OMe), 4.00 (s, 3H, OMe), 3.95 (s, 3H, OMe); **^{13}C NMR (CD_2Cl_2, 220 K, 150 MHz):** δ 177.3 (d, $^1J_{RhCO}$ = 79 Hz, CO), 171.7 (β-platinacycle), 167.3 (α-pyrr), 167.2 (meso), 165.2 (d, $^1J_{RhC}$ = 26 Hz, α-rhodacycle), 163.4 (α-pyrr), 162.9 (d, $^1J_{RhC}$ = 26 Hz, α-rhodacycle), 159.7 (para), 159.5 (para), 159.0 (para), 157.1 (α-platinacycle), 154.6 (β-rhodacycle), 150.3 (α-pyrr), 150.2 (α-pyrr), 147.8 (meso), 142.2 (β-platinacycle), 142.1 (β-pyrr), 140.0 (meso), 139.6 (α-platinacycle), 139.5 (β-rhodacycle), 139.0 (β-pyrr), 137.8 (meso), 136.9 (ipso), 136.2 (*o*-Anis), 135.8 (*o*-Anis), 135.3 (*o*-Anis), 135.0 (ipso), 134.6 (*o*-Anis), 134.5 (*o*-Anis), 134.3 (*o*-Anis), 133.8 (*o*-Anis), 128.3 (ipso), 126.6 (β-pyrr), 122.6 (β-pyrr), 114.5 (*m*-Anis), 114.3 (*m*-Anis), 112.6 (*m*-Anis), 112.4 (*m*-Anis), 112.0 (*m*-Anis), 111.7 (*m*-Anis), 55.6 (OMe); **UV-Vis (nm, logε):** 943 (3.6), 766 (3.8), 500 (4.5); **HRMS (ESI)** *m/z* = 1030.1380, calc. for $C_{49}H_{36}N_2O_5Rh^{195}Pt$, $[M\text{-}Cl]^+$: 1030.1326. **Crystal data for 5**: 6($C_{49}H_{36}ClN_2O_5PtRh$), C_6H_{14}, M = 6483.65, triclinic, P-1, a = 13.262(3) Å, b = 15.370(2) Å, c = 31.061(3) Å, α = 92.03(2)º, β = 96.66(3)º, γ = 93.88(2)º, V = 6268.3(18) Å^3, Z = 1, D_c = 1.718 Mg m^{-3}, T = 80(2) K, R = 0.0797, wR = 0.1817 (12443 reflections with $I > 2\sigma(I)$) for 1878 variables, CCDC 2241158.

Synthesis of 5-Cl_2: To the solution of **5** (10 mg, 8.8·10^{-6} mol) in $CDCl_3$ (0.6 ml) in NMR tube, chlorine gas (8.8·10^{-6} mol) was added and the mixture was shaken to give **5-Cl_2** (10 mg, 100%). Caution: chlorine gas is toxic and corrosive and must be handled according to appropriate safety rules. **^{1}H NMR ($CDCl_3$, 300 K, 500 MHz):** δ 10.08 (d, $^3J_{RhH}$ = 1.2 Hz, 2H, rhodacycle), 9.61 (s, $^3J_{PtH}$ = 51 Hz, 2H, platinacycle), 8.59 (d, $^3J_{HH}$ = 4.9 Hz, 2H, pyrr), 8.53 (d, $^3J_{HH}$ = 4.9 Hz, 2H, pyrr), 8.21 (m, 8H, *o*-Anis), 7.36 (m, 8H, *m*-Anis), 4.10 (s, 6H, OMe), 4.09 (s, 6H, OMe); **^{13}C NMR ($CDCl_3$, 300 K, 150 MHz):** δ 171.6 (d, $^1J_{RhC}$ = 25 Hz, α-rhodacycle), 170.1 (d, $^1J_{RhCO}$ = 71 Hz, CO), 160.6 (para), 160.4 (para), 159.3 (α-pyrr), 158.5 (α-pyrr), 152.3 (β-rhodacycle), 150.1 (α-platinacycle), 148.8 (β-platinacycle), 144.7 (meso), 139.6 (meso), 135.6 (*o*-Anis), 134.1 (β-pyrr), 133.9 (β-pyrr), 132.8 (ipso), 131.8 (ipso), 113.9 (*m*-Anis), 55.8 (OMe); **UV-Vis (nm, logε):** 852 (4.0), 766 (3.2), 664 (4.0), 502 (4.8); **HRMS (ESI)** *m/z* = 1101.0726, calc. for $C_{49}H_{36}Cl_2N_2O_5Rh^{195}Pt$, $[M\text{-}Cl]^+$: 1101.0702. **Crystal data for 5-Cl_2**: $C_{49}H_{36}N_2O_5Cl_3PtRh$, M = 1137.15, monoclinic, $P2_1/c$, a = 10.3888(6) Å, b = 14.6580(7) Å, c = 13.6990(8) Å, β = 99.338(6)º, V = 2058.4(2) Å^3, Z = 2, D_c = 1.835 Mg m^{-3}, T = 100(2) K, R = 0.0977, wR = 0.2593 (3326 reflections with $I > 2\sigma(I)$) for 281 variables, CCDC 2241159.

Reduction of 5-Cl_2 to 5: 10 mg of **5-Cl_2** was dissolved in CH_2Cl_2 (1 ml) after the addition of 50 mg Zn/Hg in an inert atmosphere. The mixture was stirred for 24 hours. The resulting product, **5**, was filtered through SiO_2 (8.9 mg, 95%).

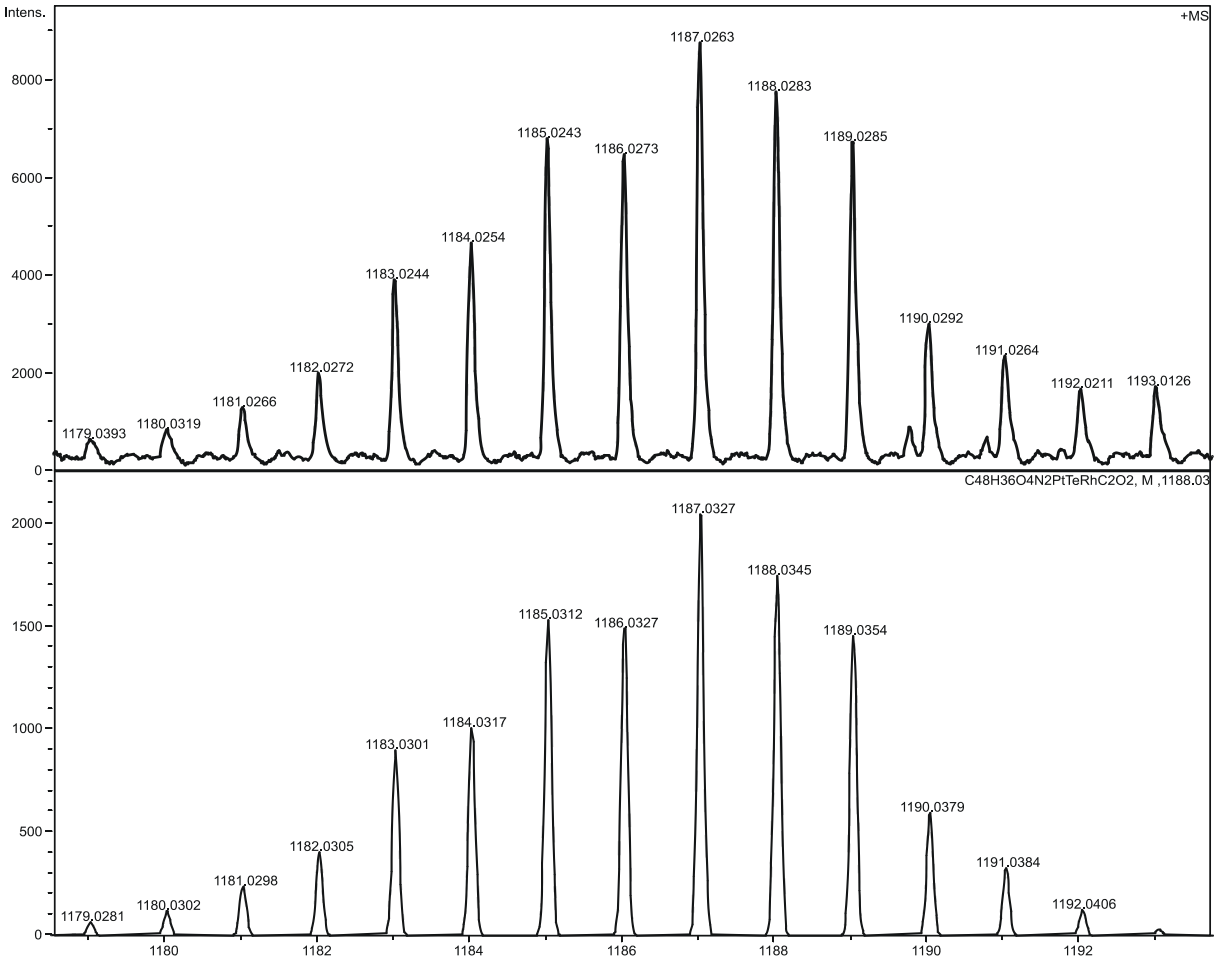

Figure S1. HRMS ESI (+MS) spectra of **4-Rh(CO)$_2$Cl**: measured (top) and simulated (bottom) calc. for $C_{48}H_{36}N_2O_4{}^{130}Te^{195}PtRh(CO)_2$, $[M\text{-}Cl]^+$.

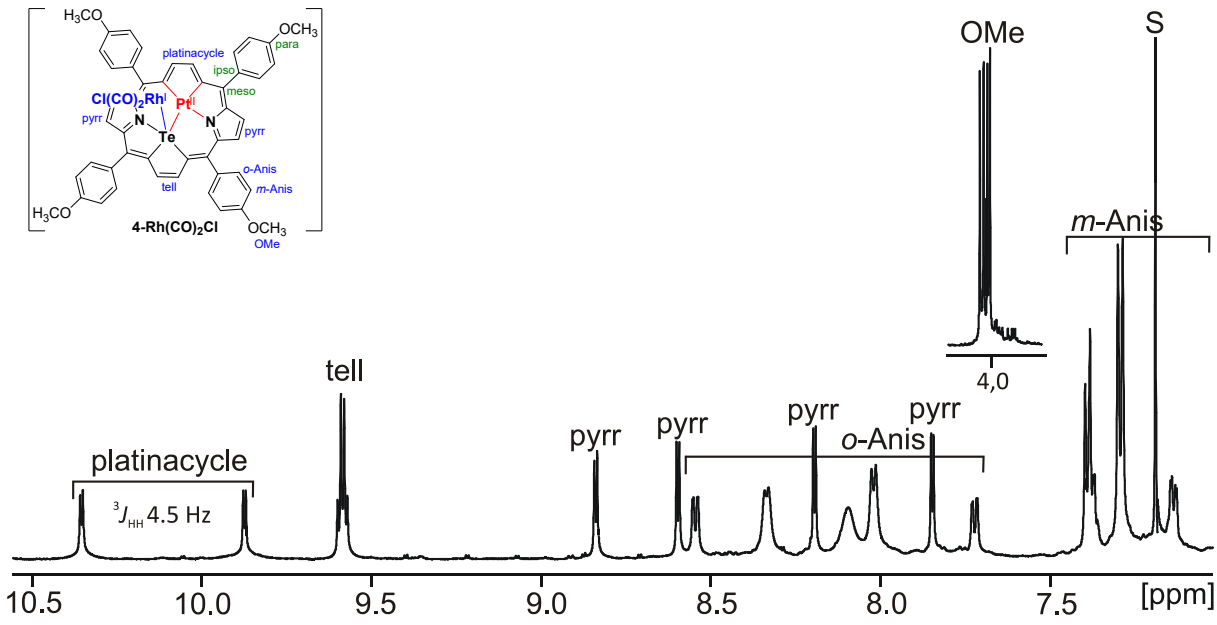

Figure S2. ^{1}H NMR spectrum of **4-Rh(CO)$_2$Cl**; 600 MHz, $CDCl_3$, 280 K.

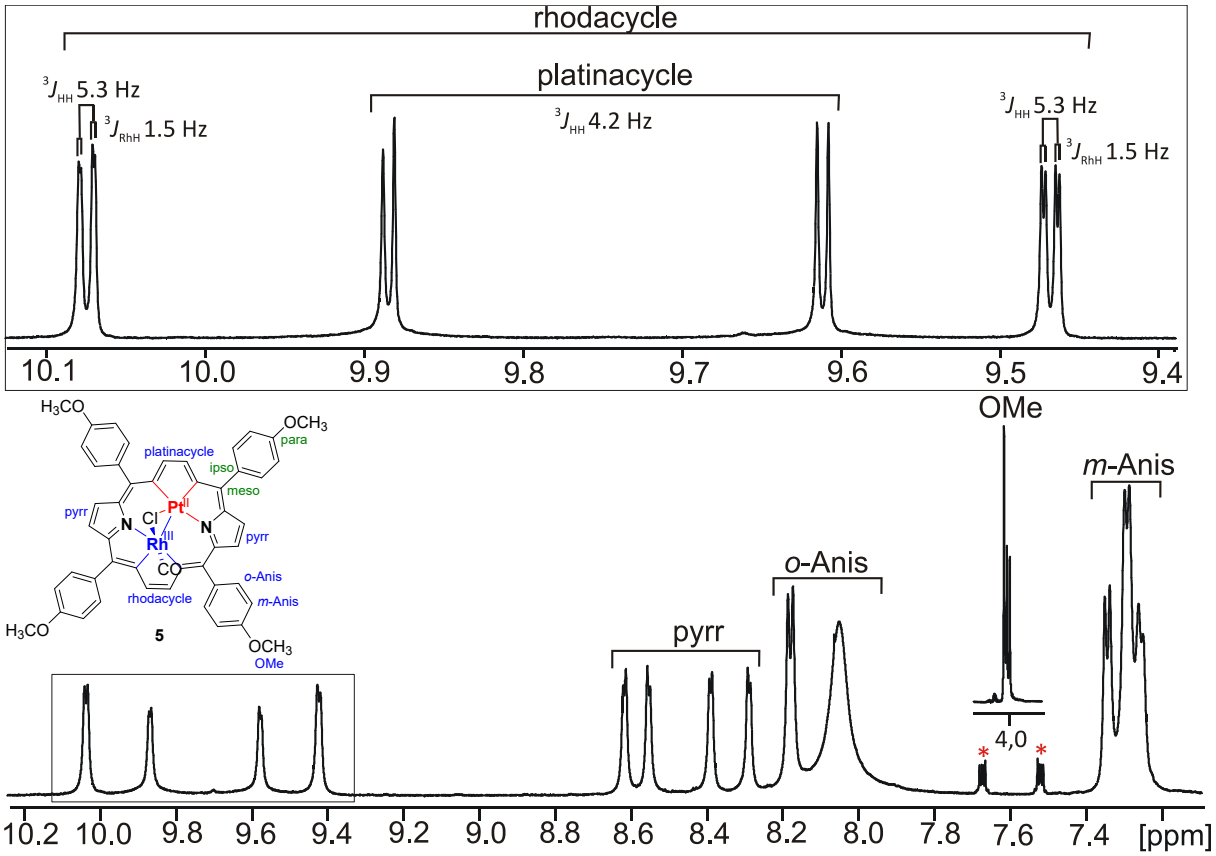

Figure S3. ^{1}H NMR spectrum of **5**; 600 MHz, CD_2Cl_2, 280 K; inset: 240 K (* = impurities).

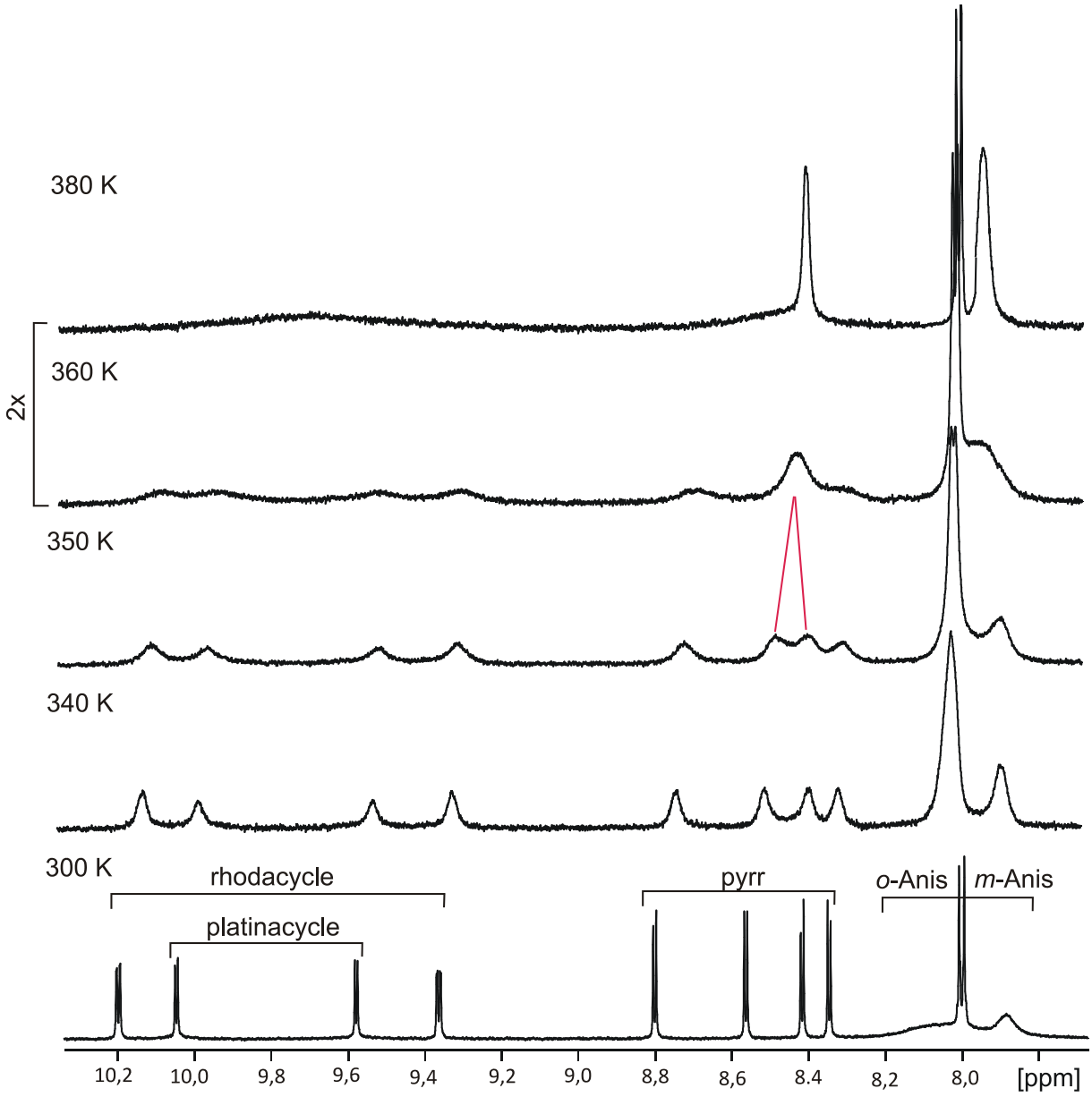

Figure S4. Variable temperature ^{1}H NMR spectra of **5**; 600 MHz, C_7D_8, 300–380 K.

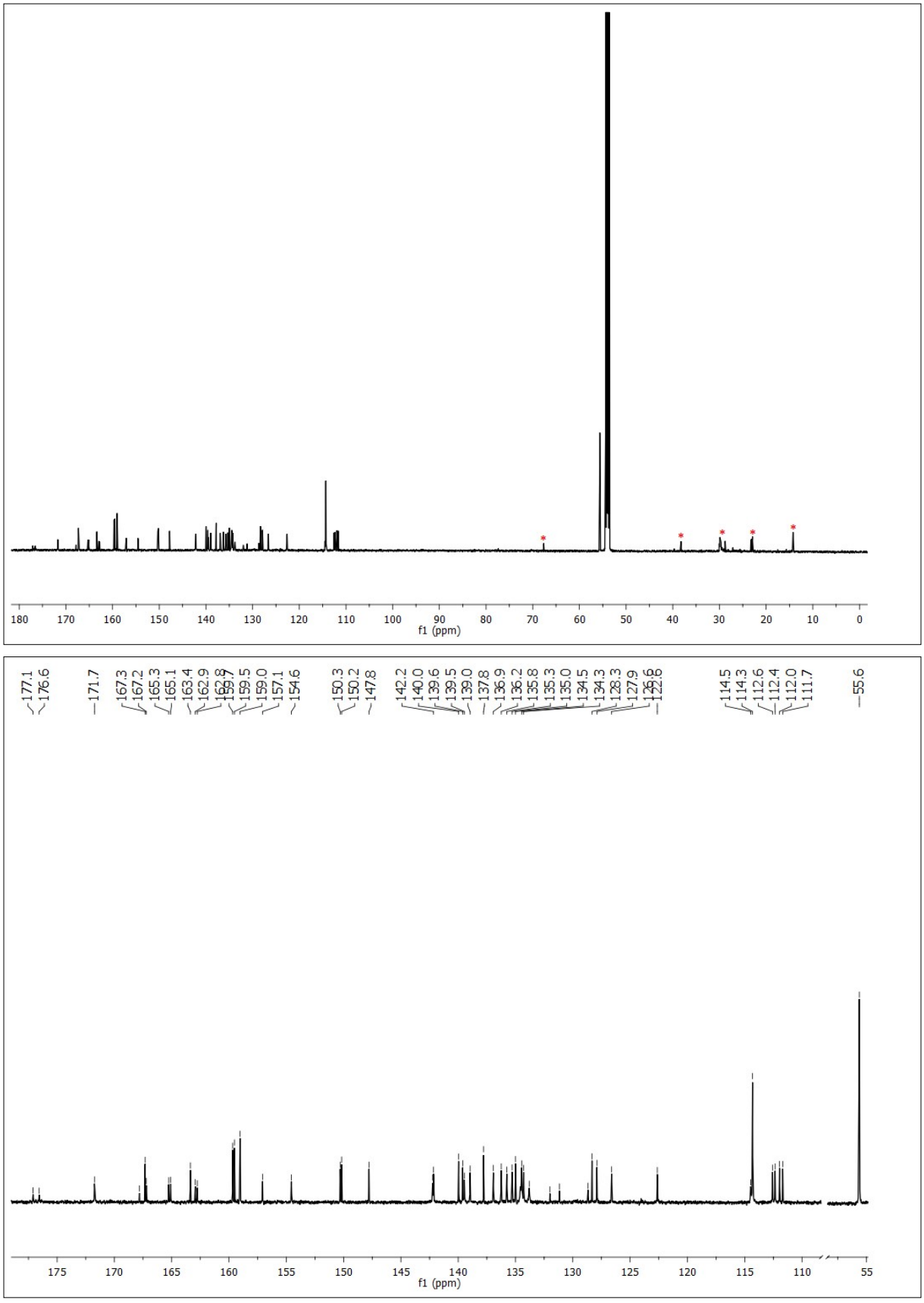

Figure S5. ^{13}C NMR spectrum of **5**; 150 MHz, CD_2Cl_2, 220 K (top: the whole spectral range, bottom: the most informative region; * = impurities).

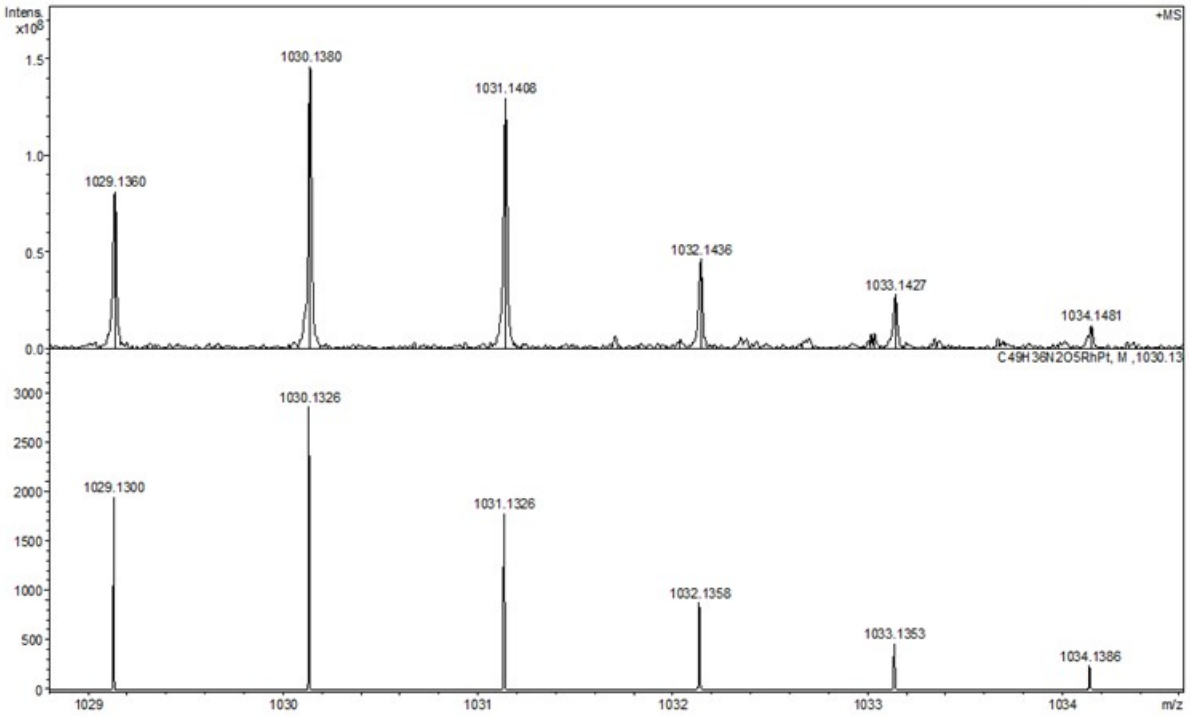

Figure S6. HRMS ESI (+MS) spectra of **5**: measured (top) and simulated (bottom) calc. for $C_{49}H_{36}N_2O_5RhPt$, $[M\text{-}Cl]^+$.

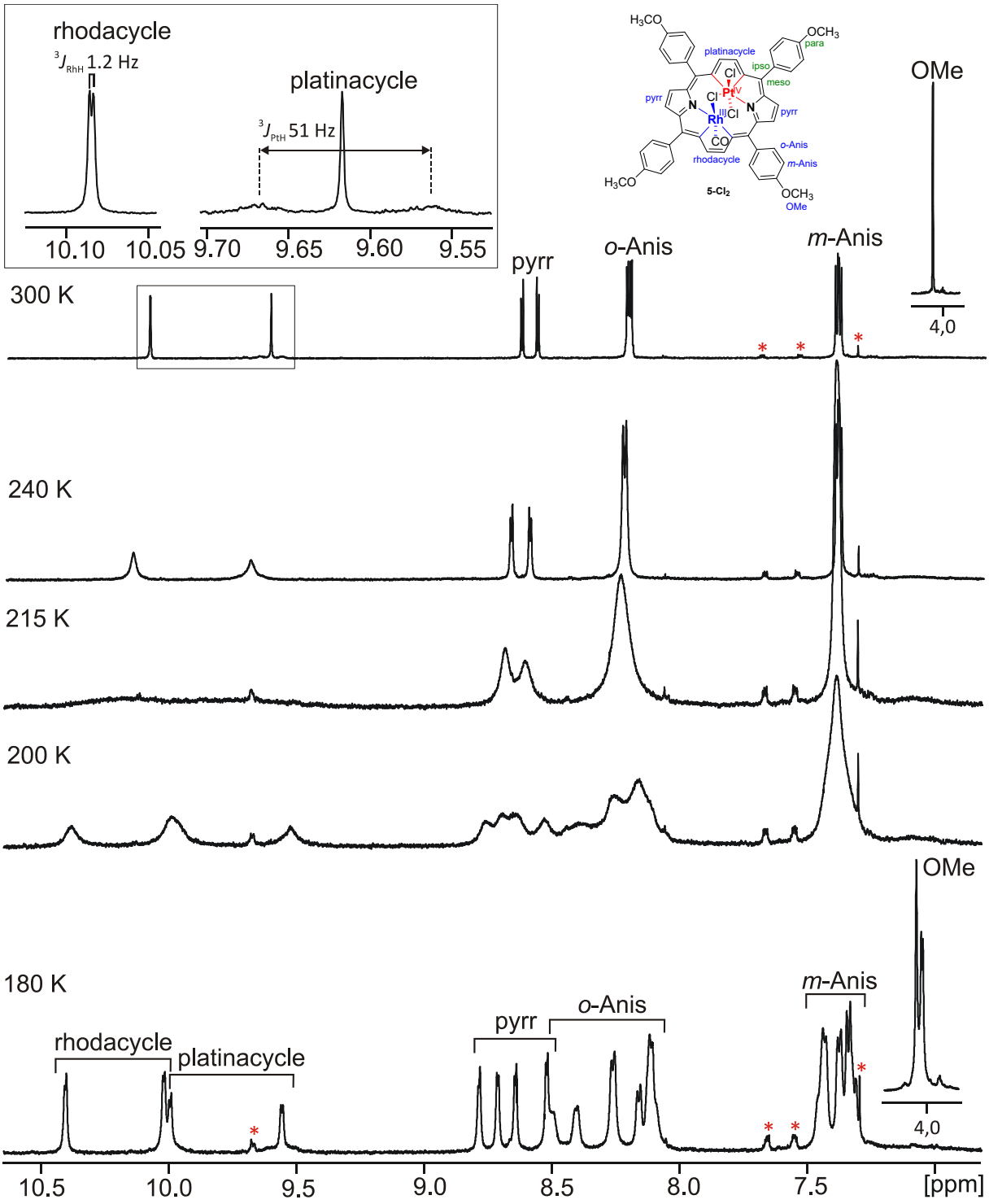

Figure S7. Variable temperature ^{1}H NMR spectra of **5-Cl$_2$**; 600 MHz, CD_2Cl_2, 180–300 K (* = impurities).

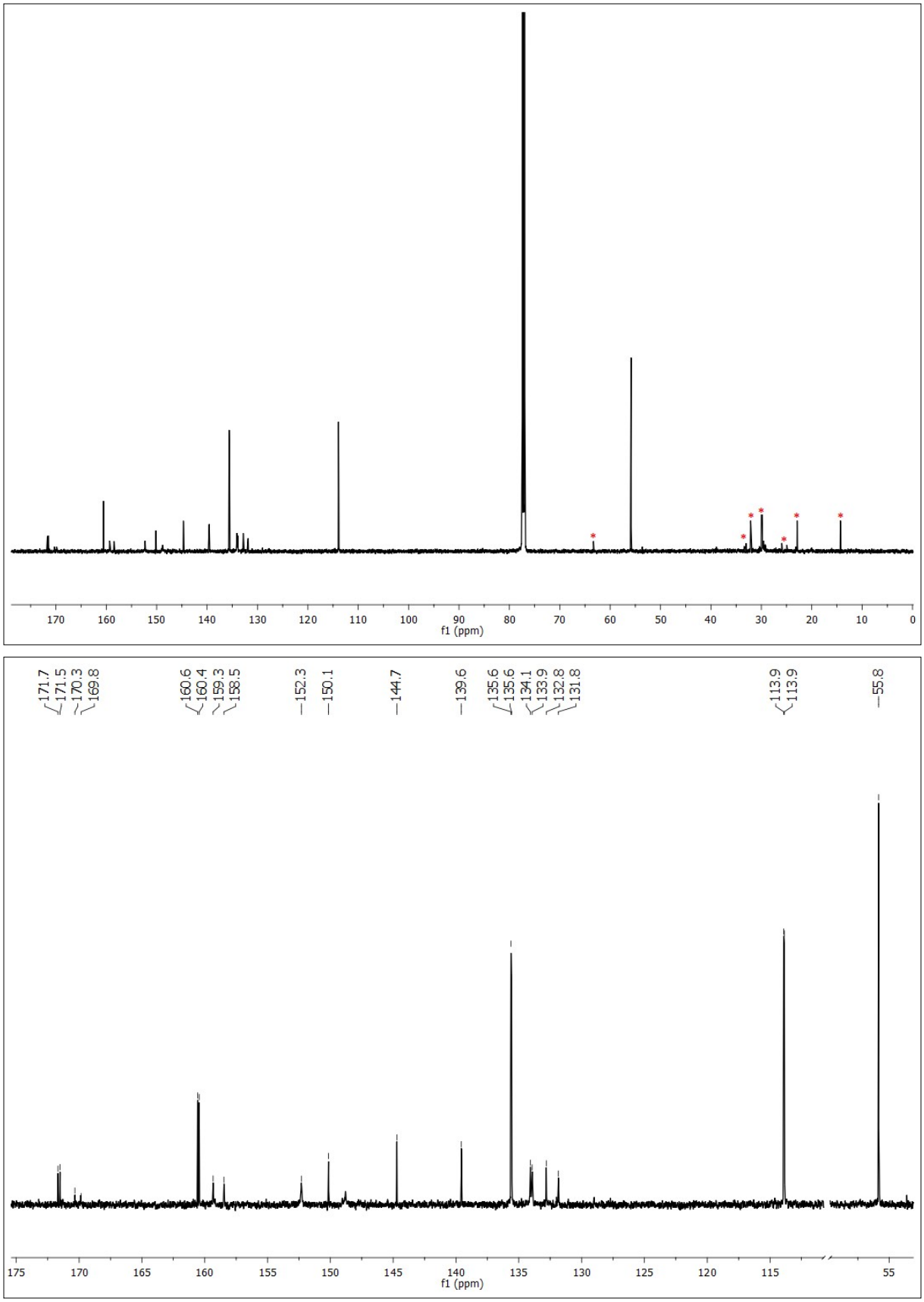

Figure S8. ^{13}C NMR spectrum of **5-Cl$_2$**; 150 MHz, $CDCl_3$, 300 K (top: the whole spectral range, bottom: the most informative region; * = impurities).

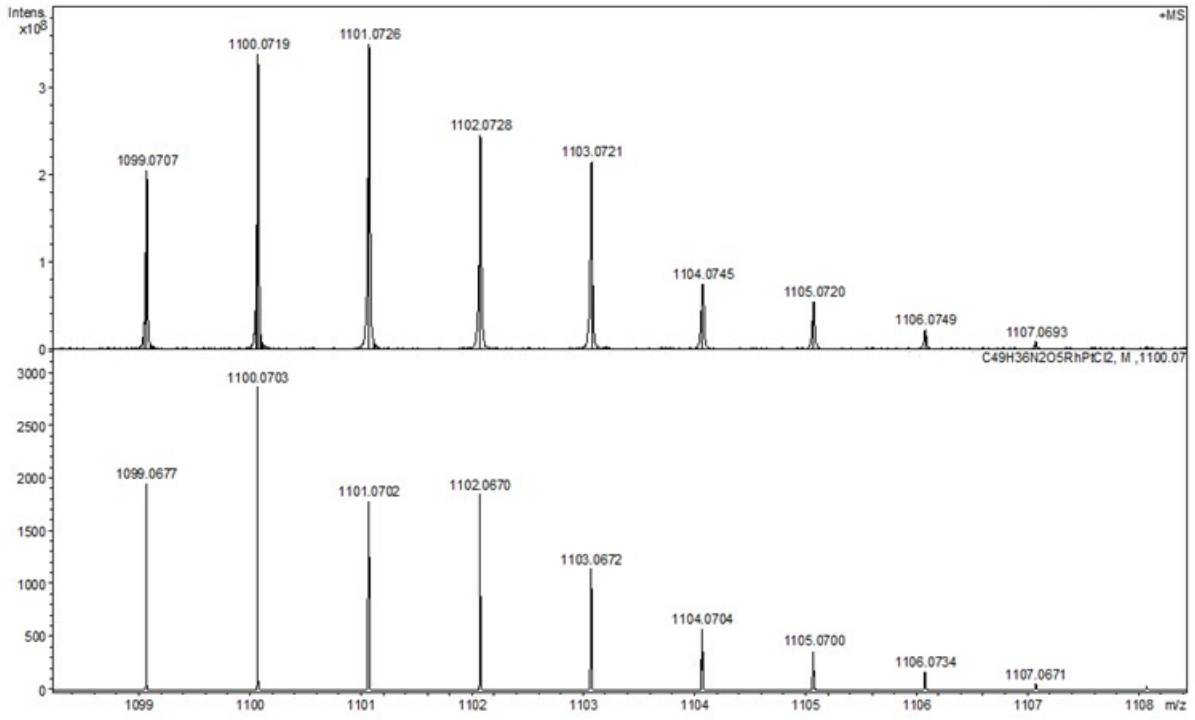

Figure S9. HRMS ESI (+MS) spectra of **5-Cl$_2$**: measured (top) and simulated (bottom) calc. for $C_{49}H_{36}Cl_2N_2O_5RhPt$, $[M\text{-}Cl]^+$.

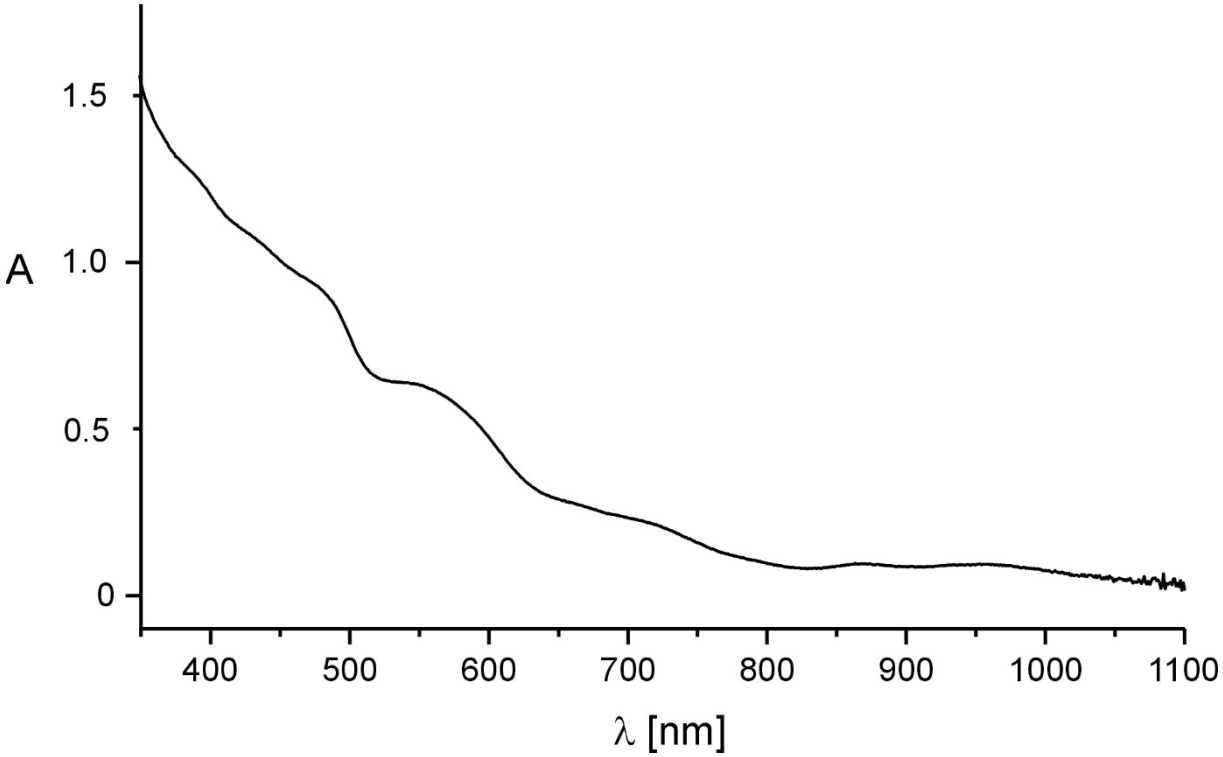

Figure S10. Absorption spectrum (CH_2Cl_2) of **4-Rh(CO)$_2$Cl**.

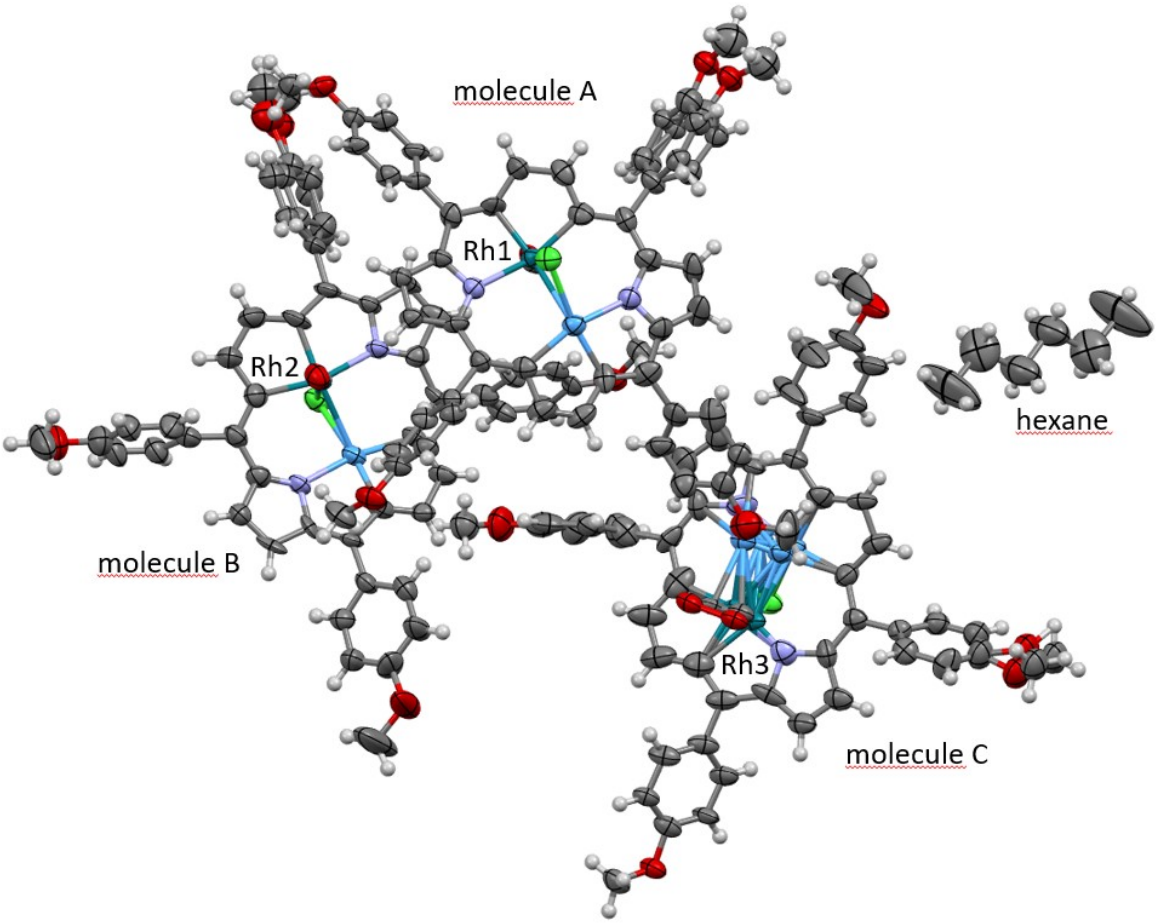

Figure S11. X-ray structure of **5**. Only molecules A and B were employed for the discussion. Displacement ellipsoids represent 50% probability.

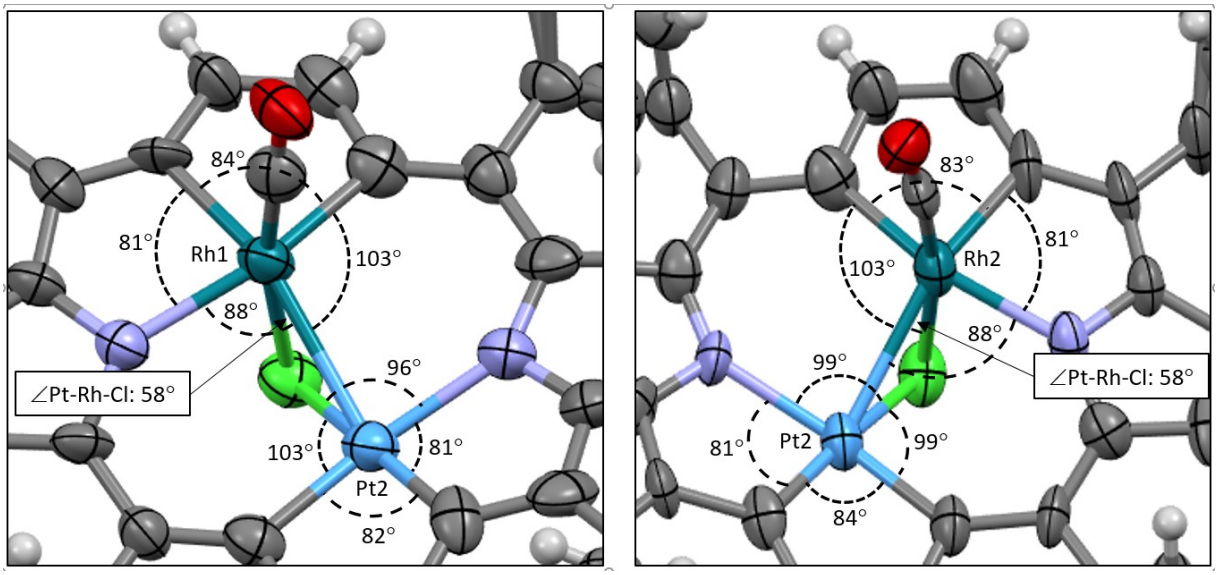

Figure S12. Angles around the central part of **5**; molecules A (left) and B (right).

3. Computational methodology

3.1. Calculations focused on metal–metal bond analysis

The initial structures for single molecules of **1**, **5** and **5-Cl$_2$** as well as for the conformational change transition states of **5** and **5-Cl$_2$** were derived from the crystal data and DFT optimization with the B3PW91 functional and mixed basis set (SDD with associated effective core potential for the metal atoms, 6-31G(d,p) otherwise). These structures were optimized at the ωB97-D3/def2-TZVP[5,6] level (the triple zeta Ahlrichs basis set also contains the effective core potentials for Pt and Rh) with default convergence settings, and the nature of the located stationary points was verified via harmonic vibrational analysis, which yielded additionally the Gibbs free energy values. The RIJCOSX approximation[7] with auxiliary basis set corresponding to the def2-TZVP basis were used to speed up the DFT calculations. The DFT calculations were carried out with the ORCA 5.0.3 program.[8] Then, the electronic structure output files from ORCA were converted to the MOLDEN format using the orca2mkl utility and further converted to the WFX standard file with the Molden2AIM package.[9] The MOLDEN and WFX files were then used for three types of analysis: Natural Bond Orbitals (NBO) description of bonding (carried out with the NBO 6.0 standalone program),[10] Quantum Theory of Atoms in Molecules (QTAIM) topological study of electron density (performed with the AIMStudio 16.10.31)[11] and Electron Localization Function (ELF) investigation (via MultiWFN 3.8 code).[12] Visualization of the QTAIM results was carried out within the AIMStudio program, while the ELF graph was prepared in GNUPlot 5.4 using data from MultiWFN.

3.2. Calculations of possible structures of 4-Rh(CO)$_2$Cl

Density functional theory (DFT) calculations were performed using the Gaussian 16 program.[13] DFT geometry optimizations were carried out in the unconstrained C_1 symmetry in vacuo, using molecular mechanics models as starting geometries. The existence of a local energy minimum was verified by a normal mode frequency calculation. DFT calculations were performed using the hybrid functional b3pw91 and a combined basis set consisting of SDD pseudopotential for Rh, Te, and Pt atoms and 6-31G(d,p) for the remaining atoms. Such a functional and basis combination has properly modelled the macrocyclic geometries in our previous work with 21,23-dirhodaporphyrin.[14] All relative energies include the zero-point correction.

4. Computational results

4.1. Energetic and structural considerations

The energetic parameters of the optimized structures, contained within Table S1, indicate that the conformational dynamics in **5** is much slower as compared to **5-Cl$_2$**. The barrier estimates, given by the relative energies of the conformational transition states, are in relatively good agreement with the experiment (consistently 3 kcal/mol higher barriers than from the NMR experiment), which is carried out in a solvent, while the gas phase models are used in

calculations. The role of thermal corrections (zero point vibrations, rotational terms) is very small.

The metal–metal separations can be significant for explanation of the barrier heights. Relatively short Pt–Rh distance (2.715 Å) in **5**, comparable to the Pd–Pd distance of 2.67 Å found in a *cis*-bimetallic complex of dinaphthoporphycene,[15] suggests some degree of metal–metal bonding, which will be investigated in the following paragraphs. This is not the case for **1** and **5-Cl$_2$**, but interestingly the conformational transition state of **5-Cl$_2$** has the Pt–Rh distance significantly shortened (from 2.995 to 2.766 Å), already comparable to **5**. Thus, the **[5-Cl$_2$]**‡ structure can be potentially stabilized by the metal–metal interaction, lowering the barrier. Conversely, the metal–metal distance in **[5]**‡ (2.658 Å) might be sterically forced, and already in the repulsive regime, destabilizing this structure and heightening the barrier. It is important to note that for **1** the barrier is small enough to warrant fast NMR exchange; the computational estimate is also decidedly smaller than for the Pt–Rh compounds. The barrier height is inversely correlated with the shortening of the metal–metal distance between the minimum and the transition state. This shortening is most pronounced for **1** (from 2.962 to 2.708 Å – by 0.254 Å), quite significant for **5-Cl$_2$** (by 0.229 Å) and least visible for **5** (by 0.057 Å); the metal–metal distance in **[1]**‡ is even smaller than in the **[5]**‡, but the barrier is very low – this fact suggests that the reason for barrier lowering is the presence of metal–metal bonding in the transition state. The structure **5** contains such bonding already before reaching the transition state (see the discussion below), therefore it does not gain any stability in the transition state.

Table S1. Energies of the optimized structures of **1**, **5** and **5-Cl$_2$** together with the metal–metal distances. Results of ωB97-D3/def2-TZVP calculations. Gibbs free energies are electronic energies corrected for harmonic vibrational and rotational terms at 298.15 K and 1 atm.

	1 (Rh–Rh)	**[1]**‡ (Rh–Rh)	**5** (Pt–Rh)	**[5]**‡ (Pt–Rh)	**5-Cl$_2$** (Pt–Rh)	**[5-Cl$_2$]**‡ (Pt–Rh)
d(M_1–M_2) [Å]	2.962	2.708	2.715	2.658	2.995	2.766
d(M_2–M_2) [Å] (X-ray)	2.867(1)		2.6972(12) 2.7172(13)		2.911(6)	
Total Energy [Ha]	–3629.69232582	–3629.67869195	–3064.90711962	–3064.87401216	–3985.35782358	–3985.33667804
Gibbs free energy [Ha]	–3629.02980878	–3629.01744325	–3064.25346656	–3064.21935939	–3984.70264711	–3984.68136543
Relative energy [kcal/mol]	0	8.5	0	20.8	0	13.3
Relative Gibbs free energy [kcal/mol]	0	7.7	0	21.4	0	13.4
Exp. (NMR) barrier [kcal/mol]		small (fast NMR exchange in the available temp. range 300-175 K)		17.4(5)		9.4(2)

4.2. Metal–metal bonding – QTAIM and ELF description

The presence of metal–metal interaction in a single molecule cannot be easily studied using supramolecular approach, *i.e.* by decomposing the structure into two separate parts and calculating the interaction energy between them. We resort to other methods of electronic structure analysis. In particular, Quantum Theory of Atoms in Molecules (QTAIM)[16] was found useful in understanding interatomic bonding schemes including metal–metal bonds.[17] The topology of electron density close to the metal centers is presented in the Figure S13, while the parameters of the most relevant Bond Critical Points (BCPs) are given in Table S2. Table S3 provides data on several BCPs in the structure of **5**, so that the metal–metal BCPs can be put in the perspective of other bonds.

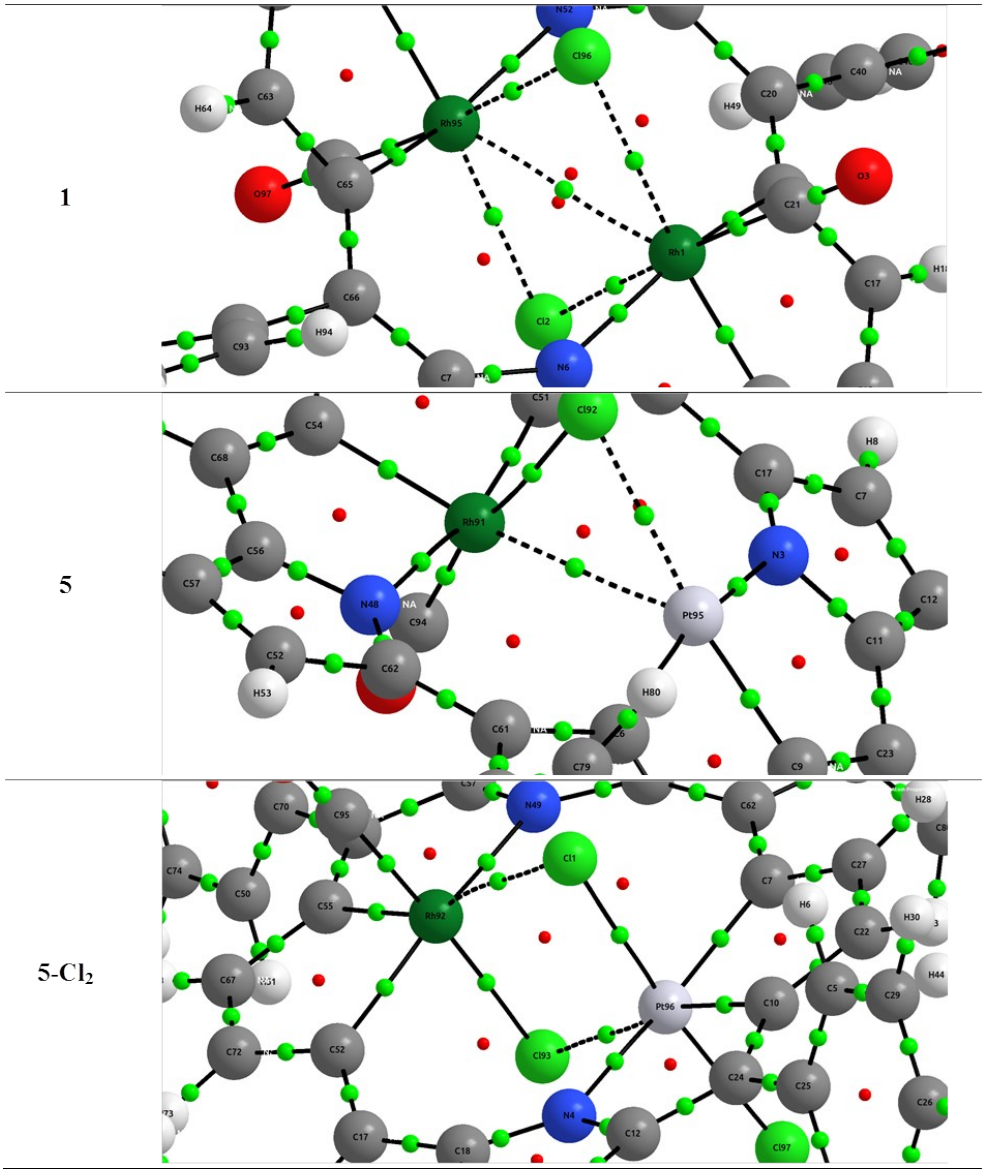

Figure S13. Topology of electron density in the vicinity of metal centers of **1**, **5** and **5-Cl$_2$** – results of QTAIM analysis. Atom color coding: dark green – Rh, silver – Pt, grey – C, white – H, blue – N, red – O, green – Cl. Critical point color coding: green – bond critical points (BCP), red – ring critical points (RCP). The atoms are connected with QTAIM bond paths. Low values of electron density at a particular BCP are signaled by dashed bond paths.

Table S2. QTAIM parameters of the metal–metal bond critical points.

	1	**5**	**5-Cl$_2$**
d(M_1-M_2) [Å]	2.962	2.715	2.995
ρ [a.u.]	0.0264	0.0463	---
Laplacian of ρ [a.u.]	+0.0613	+0.1251	---
Ellipticity	1.665	0.190	---
d(BCP-RCP) [Å]	0.316	0.473	---

Table S3. QTAIM parameters of selected BCPs in **5**.

	Pt–Rh	**Pt–N**	**Rh–N**
ρ [a.u.]	0.0463	0.1077	0.0866
Laplacian of ρ [a.u.]	+0.1251	+0.3754	+0.3471
Ellipticity	0.190	0.061	0.093
	Pt–Cl	**Rh–Cl**	**C6–C26**
ρ [a.u.]	0.0623	0.0735	0.3257
Laplacian of ρ [a.u.]	+0.1916	+0.2320	–0.9567
Ellipticity	0.103	0.108	0.212

The data presented above indicate that the structure of **5-Cl$_2$** does not exhibit a Pt–Rh BCP, while the structure of **1**, with very similar metal–metal distance, does have a Rh–Rh BCP and associated interatomic path. The structure of **5** also contains a metal–metal BCP. The QTAIM suggests, at the first glance, that metal–metal bonding might be present in **1** and **5**. Comparison of the BCP properties (Table S2) shows that the electron density ρ and its Laplacian for the BCP of **1** are only two times smaller than in **5**, despite large difference in the metal–metal distance. However, there is large disparity between the ellipticity values. Ellipticity is a parameter associated with distortion of the electron density in the plane perpendicular to the bond path at the BCP. Ellipticity values are large for double bonds (C=C, C=O etc., attaining 0.23 for benzene and 0.45 for ethene),[16] which is obviously not the case here, and also in situations of very low electron density at the BCP, not really indicative of bonding, but rather due to sterically forced atom–atom proximity. We consider **1** to be such a case. Small structural changes would then lead to coalescence of the bond and ring critical points (see the green and red dots on Figure S13) into a new ring critical point, leading to the situation found in **5-Cl$_2$**. The BCP–RCP distance in **1** is shorter than in **5**, supporting this reasoning.

The Pt–Rh BCP in **5** has electron density of only 0.0463 a.u., which is an order of magnitude smaller than the ρ for covalent bonds (see Table S3), but comparable to the values found in hydrogen bonds and coordination bonds – the Table S3 shows that both ρ and its Laplacian are ca. two times larger for the Pt–N, Rh–N, Pt–Cl, Rh–Cl contacts. The covalent C–C bond is markedly different from the other contacts, also due to different signs of the Laplacian of ρ. These data suggest the existence of weak, but not accidental Pt–Rh contact in **5**, but not in **1** or **5-Cl$_2$**. Further evidence of this is given by the profile of Electron Localization Function (ELF) between the metal atoms (Figure S14). While for **1** and **5-Cl$_2$** the ELF between the metal

atoms drops uniformly, there is a distinct shoulder of the ELF for **5** suggesting a change of bonding pattern. No new nodal structure (new minima and maxima) is formed, therefore significant covalent interaction should be excluded on the basis of the ELF analysis, and weaker metal–metal contact should be considered.

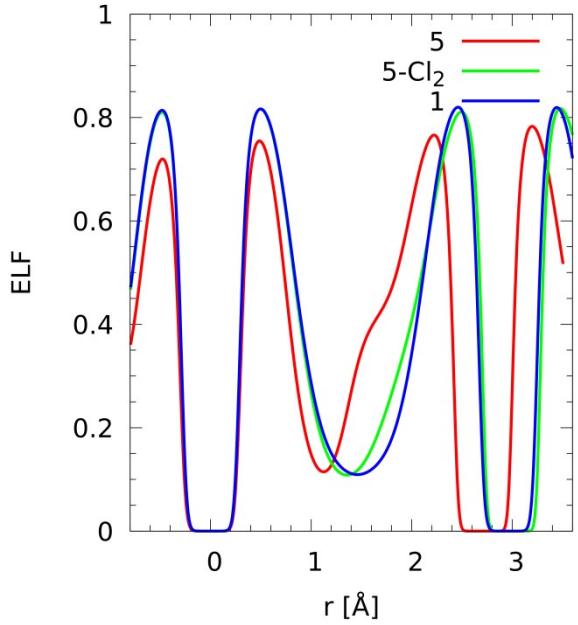

Figure S14. Electron Localization Function (ELF) along the metal–metal line in **1**, **5** and **5-Cl$_2$** – the Rh atom is at coordinate 0 Å, and the second metal atom (Pt/Rh) is at the minimum of the well at 2.7–3.0 Å.

4.3. Natural Bond Orbital (NBO) parameters for the metal–metal bonding

The discussion above is based on the topological analysis of electron density and related functions (ELF). It is also necessary to consider the wavefunction-based arguments. In the following text, we will use the terms 'wavefunction' and 'orbitals' keeping in mind that these are in fact Kohn-Sham determinant and Kohn-Sham one-electron wavefunctions respectively.

The Natural Bond Orbitals methodology transforms the LCAO MO orbitals into a series of well-defined orbital types maximizing their localization or occupation number.[18] The resulting orbitals represent the dominant Lewis structure, and their properties are less basis-set dependent than raw LCAO MO orbitals. The parameters listed in Table S4 allow for estimating the metal–metal bond order. The Wiberg bond index (calculated from standard orbitals, not NBO) is a measure of electron population overlap between two atoms, or an average number of electron pairs shared by both atoms. In our study, the Wiberg bond index is reported in the NBO spirit, *i.e.* calculated within the Natural Atomic Orbitals basis. Its value, while not close to 1 (ideal single bond), is markedly higher for **5** than for the other considered molecules, in agreement with the discussion above. It is also very close to the value of 0.18 found in a *cis*-bipalladium complex of dinaphthoporphycene,[15] suggesting similarity of the bonding schemes in the two cases. The bond index calculated from the NBO-derived natural localized molecular orbitals (NLMOs) is very similar in magnitude. Concluding, the computational methods

indicate the presence of metal–metal (Pt–Rh) interaction in **5**, which is however weaker than a formal single metal–metal bond. The NLMO/NPA bond orders are much increased in the transition states, once more suggesting important role of metal–metal interactions in determining the conformational flexibility of the studied systems.

Table S4. NBO parameters for the metal–metal interactions and metal atom net charges.

	1 (Rh–Rh)	**5** (Pt–Rh)	**5-Cl$_2$** (Pt–Rh)
Wiberg Bond Index	0.0405	0.1528	0.0318
Linear NLMO/NPA Bond Order	0.0452	0.1482	0.0418
q(Rh)	0.439	0.475	0.433
q(Pt / Rh)	0.436	0.587	1.004
	[1]‡ (Rh–Rh)	**[5]**‡ (Pt–Rh)	**[5-Cl$_2$]**‡ (Pt–Rh)
Wiberg Bond Index	0.0687	0.0842	0.0609
Linear NLMO/NPA Bond Order	0.1142	0.1591	0.1306

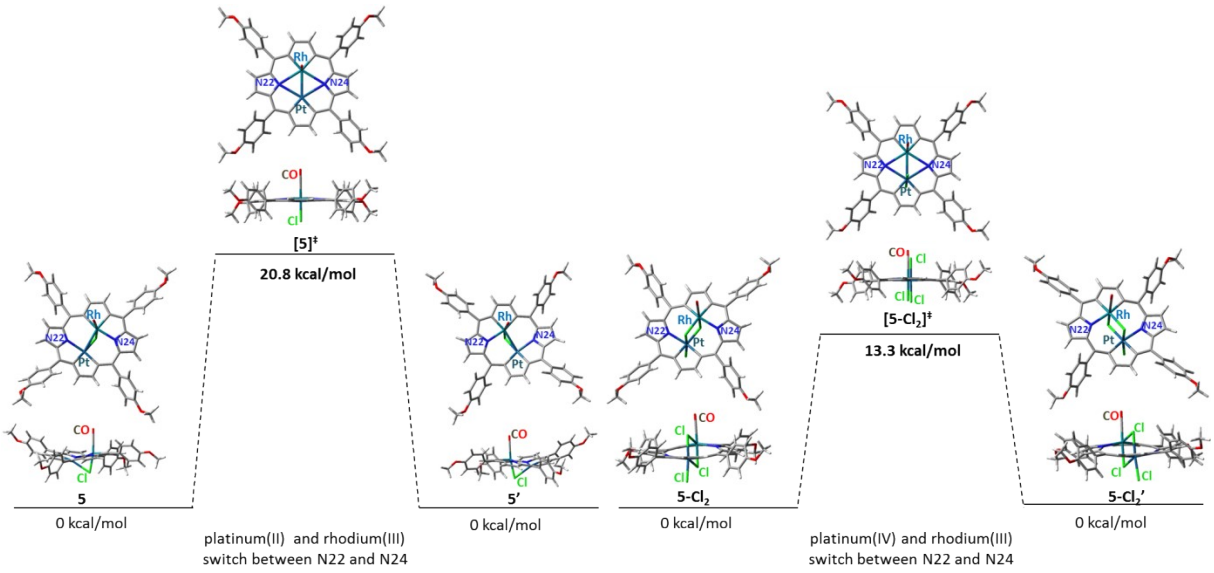

Figure S15. Energy diagram for conformational interconversions of **5** and **5-Cl$_2$**.

4.4. Calculations of possible structures of 4-Rh(CO)$_2$Cl

The structure of an intermediate product **4-Rh(CO)$_2$Cl** is proposed on the basis of ^{1}H NMR analysis (C_1 symmetry, aromaticity), HRMS spectrometry (detection of [**4-Rh(CO)$_2$**]$^+$ ion) and by analogy to the literature example (coordination of Rh(CO)$_2$Cl unit to a monodentate site of N-confused porphyrin).[19] Two heteroatoms available for rhodium(I) binding, tellurium and nitrogen, were taken under consideration. Thus, calculations were performed for six models presented in order of increasing energy in Figure S16. In three of the hypothetical structures (No. **1**, **2** and **5**), rhodium(I) is attached to the tellurium atom, while in the remaining structures, rhodium(I) is linked to the nitrogen atom, not engaged in platinum coordination. Furthermore,

the structures differ in chloride and carbonyl ligands arrangement, and the results of the calculations show, that the cis arrangement of two CO ligands has lower energy, as expected.[20] Two pairs of isomers may be regarded as pairs of rotamers (No. **1** and **2**; No. **3** and **4**). We assume, that the most probable structure of **4-Rh(CO)$_2$Cl** is the structure **4**-Rh(CO)$_2$Cl-**1** and its rotamer **4**-Rh(CO)$_2$Cl-**2**.

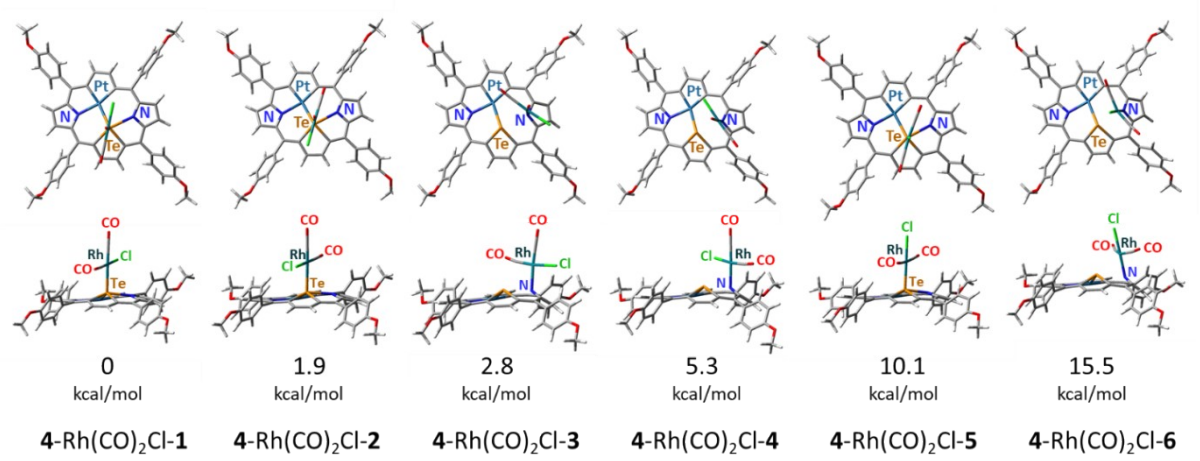

Figure S16. DFT-optimized structures of possible isomers of **4-Rh(CO)$_2$Cl** and their relative energies.

Table S5. Cartesian coordinates of DFT (ωB97-D3/def2-TZVP) optimized structures of **5** and **5-Cl$_2$**.

Coordinates for **5**

O	-0.98750526011586	-8.82239473498507	-1.06751418458965
O	9.23951075404538	-0.55343181731108	1.76822878192417
N	1.84819156873484	-1.70518913419292	-0.53929851741664
C	5.63097663500529	0.09946317246409	1.67759364931849
H	4.85997314878572	0.60415997772078	2.24711279109396
C	1.20521457746138	2.29233966629310	-0.57281866162654
C	2.40026096903527	-3.85303198988872	-0.08741085524915
H	2.26061431546662	-4.91228035920883	0.06116080315340
C	3.09804428989005	0.57432670554579	-0.10258887603182
C	-0.75957105421950	-7.48945378429028	-0.97154919956156
C	3.20925233904417	-1.77824133195497	-0.20640662719913
C	3.55035721697822	-3.14633046961654	0.03295665197259
H	4.52452393375900	-3.50946834258371	0.32045581780720
C	-0.42687862036307	-6.66771868100075	-2.04151934837736
H	-0.33394758707662	-7.06394635239574	-3.04319514764588
C	-0.06944028958597	-3.29266581782553	-0.34728334544707
C	1.33604354684559	-2.91792452438536	-0.38965249955697
C	-0.20995833854226	-5.31207268610694	-1.82406304237653
H	0.04881163863362	-4.67556892909231	-2.66283653342982
C	-0.32405059576417	-4.75199077597411	-0.56117004688192
C	3.48215940886347	1.87883750196980	0.00278473215198
H	4.48685026396811	2.18904495337467	0.27288433646516
C	3.88244190056110	-0.60811056845118	0.05729957922931
C	5.28154195069418	-0.58604954306577	0.52065461053207
C	7.93323191144992	-0.52895561546791	1.41859463356047
C	2.43505649975856	2.81729685142611	-0.23198132645435
H	2.59263868498553	3.87572520857662	-0.04906603057243
C	6.94042379156344	0.13131432812752	2.13355483382797
H	7.16858017553686	0.66814834587787	3.04367798847033
C	-0.86928143685147	-9.42940857745374	-2.33271942651605
H	-1.07310042776550	-10.48703980490550	-2.18083659397114
H	0.13925227130608	-9.31356832214555	-2.74212341192367
H	-1.59564702410960	-9.02256607285357	-3.04354850292100
C	-0.65677905685888	-5.59395222477872	0.50086047667205
H	-0.74187965688881	-5.17656250440673	1.49802196292321
C	7.59738820274965	-1.22199020936464	0.25627853411128
H	8.38365701259176	-1.72564983205309	-0.29143627610552
C	-0.87417383329132	-6.94203845511107	0.30506892204054
H	-1.13094025155102	-7.59579280487140	1.12921092246500
C	6.29084087176744	-1.25053658856112	-0.18080136135567
H	6.04282029808604	-1.77862575894677	-1.09404926245654
C	9.63328410982479	0.15250694376756	2.92335127355767
H	9.14746039465013	-0.24462466352689	3.81999302424042
H	9.41231311257970	1.22055526423843	2.83381598633052
H	10.70859294390636	0.01563437021966	3.01024304595095
O	1.00603962318776	8.58053871544156	-1.92564921235486
O	-9.28898265253839	0.78739130402057	1.51113808987640
N	-1.65174486832054	1.62574685467336	0.29678770445606
C	-6.08144207284569	-0.00066019556285	-0.09726360466372
H	-5.68895520973559	-0.46881297188981	-0.99255189623414
C	-1.08165241953477	-2.44805877742312	-0.02336428464806
C	-2.35238623697173	3.75480248663096	-0.15196368863408
H	-2.32983068997189	4.78671216023140	-0.46249574414501
C	-3.01418874985870	-0.65954787564038	0.49913949287213
C	0.77756208777148	7.31615658242370	-1.50027845064568
C	-2.96797929564132	1.69933764057445	0.45366756580437
C	-3.43916678502806	3.03641548008502	0.21162867766821
H	-4.46809097909825	3.35745902348010	0.25529601992186
C	0.31760534322848	6.98324315397173	-0.23243343757594

H	0.12842476606233	7.74256209078241	0.51353478144095
C	0.07771041532356	3.20552467296732	-0.50001736361245
C	-1.20206615523433	2.86988813182446	-0.12101732717994
C	0.09658933193272	5.64924676914644	0.08753824818885
H	-0.25890003441763	5.39509379788437	1.07916395614668
C	0.33372645649246	4.63366558235407	-0.82796393090981
C	-3.42067372798189	-2.03075532215237	0.40751630327099
H	-4.46238846791272	-2.31452082444376	0.51443349162345
C	-3.72965566270012	0.48545006424413	0.62888140729478
C	-5.19913536488471	0.54583176989056	0.82271938838739
C	-7.96965702144528	0.67697619812512	1.22397442320865
C	-2.45142949044286	-2.92274802862867	0.11253049501523
H	-2.68867192841773	-3.97072175441082	-0.03401934784834
C	-7.45739547137693	0.05619567962735	0.09196233825953
H	-8.11094651354376	-0.37786180719698	-0.65194501642975
C	0.69989974310389	9.64310787768498	-1.05254478465341
H	0.92620534373093	10.55713392265790	-1.59664843159102
H	-0.35955781706087	9.64070389981489	-0.77753097227131
H	1.30883951456889	9.60632332677114	-0.14380881437941
C	0.83005151172122	4.98565548407181	-2.08627229284533
H	1.03426072027684	4.20653850884199	-2.81089348103924
C	-7.09547037898033	1.24159265429336	2.15184657054729
H	-7.51090317782228	1.72206904961943	3.02875699431737
C	1.03829478084260	6.30420470855181	-2.42466829277453
H	1.40009381370926	6.58093885344694	-3.40673387135723
C	-5.73418958391182	1.17653515222056	1.94899868069164
H	-5.06390615477534	1.61394965576802	2.68064482994021
C	-10.21603765025746	0.24621853998176	0.59885842453028
H	-10.13779677426641	0.72442295730886	-0.38257031177419
H	-10.08335319600723	-0.83444747350130	0.48599008943966
H	-11.20156379328089	0.44324471702530	1.01476745368644
Rh	-1.06963380361135	-0.43225374793583	0.26036186485462
Cl	-0.83671795291070	-0.11324482115903	-2.08748792632222
O	-0.76840648422051	-0.97507536559684	3.16256868747358
C	-0.89674360962831	-0.75393302930056	2.05864028422229
Pt	1.30011341713979	0.29554951557897	-0.84575705938155

Coordinates for **5-Cl$_2$**

Cl	1.20791330205445	0.27305366624592	1.90806775753797
O	-1.02313980221314	-8.66146383114889	-1.00879648174566
O	9.50935967063793	-0.73838394511348	0.99512761162598
N	1.86957554729378	-1.67122714004569	-0.26915369119309
C	5.95636955450917	0.10617915031357	1.33064139370002
H	5.28603965354832	0.65153705425242	1.98441913573534
C	1.23213781157510	2.35714686376494	-0.23612210078627
C	2.44245876708076	-3.78210756366957	0.27866824255794
H	2.30533502120957	-4.82460873306848	0.51926347588352
C	3.25053129224117	0.64878742921725	-0.12381433743941
C	-0.77390673483088	-7.34761692152274	-0.78923973563953
C	3.26015379915108	-1.73828847697552	-0.10883946289147
C	3.60593900914097	-3.10079717758723	0.19856600272755
H	4.60364500832392	-3.46786095001470	0.38093496443203
C	-0.51010734829342	-6.41909990035815	-1.78875297647876
H	-0.48871723899004	-6.70838061636454	-2.83022788707155
C	-0.05531567668204	-3.22296346435921	0.19659018920255
C	1.35228371917291	-2.84276957383743	0.03830711960585
C	-0.27324998499097	-5.09316356830523	-1.44860727482868
H	-0.07456008577082	-4.37129976211477	-2.23305901235288
C	-0.30044525672435	-4.66633399542534	-0.12988098063233
C	3.58598267262949	1.95522567025836	-0.03898560970379
H	4.60915301375460	2.28873350569909	0.09379590704319
C	3.98758594305682	-0.57820995925924	-0.02752152895618
C	5.43723458772730	-0.58238158631174	0.24193623981431
C	8.17510890997288	-0.64357003588841	0.80213805860920
C	2.48686213338074	2.87780898667988	-0.08651809239163
H	2.65637446781768	3.93642030948578	0.07457092543968
C	7.31261177975747	0.07912761130941	1.61947119811839
H	7.67780538630126	0.61338514288682	2.48524524940140
C	-1.03303048270429	-9.12327418713884	-2.33973899345339
H	-1.26060825369152	-10.18571881308331	-2.29023392363574
H	-0.05881028954513	-8.98719456732933	-2.81963599493738
H	-1.80180008404400	-8.61755691046512	-2.93246358002364
C	-0.55689753490128	-5.61396661466561	0.86112875782695
H	-0.57484349594188	-5.30214592587520	1.89966730582793
C	7.66651736873458	-1.32912751280956	-0.30056615091919
H	8.35261438878265	-1.87841673853091	-0.93243422093341
C	-0.79252891350569	-6.93589388986090	0.54218341587574
H	-0.99484150851947	-7.67170792704666	1.31045018280198
C	6.31596087037809	-1.30031193214711	-0.57173642448902
H	5.92813057347023	-1.82425749921992	-1.43728603697995
C	10.07486747468850	-0.06975658710466	2.10049305013442
H	9.66569277821607	-0.44255482775478	3.04452445100064
H	9.91719919303220	1.01128455496220	2.03765488721155
H	11.14155510191939	-0.27821287443998	2.06589233529553
O	0.88410165013546	8.53280809671190	-1.70579832163266
O	-9.46019749946018	0.75422726901915	0.60140142939447
N	-1.73133355429184	1.63195360443622	0.75475902284467
C	-6.01280109076491	-0.11695513592945	-0.31975154045199
H	-5.46337526489025	-0.64704908990182	-1.08909184588246
C	-1.08992583079218	-2.43479156157508	0.59833045426579
C	-2.38075503173230	3.71400969041262	0.05192660381066
H	-2.32343497659205	4.72022213288610	-0.32934248209217
C	-3.10713393503355	-0.67956682792612	0.77877843369579
C	0.67091096906324	7.28063352073853	-1.24083154261467
C	-3.05619128517074	1.68595918908965	0.68446259841084
C	-3.49900981245738	3.00051462088594	0.29092197912000
H	-4.52515936530988	3.30086819173752	0.14969041146727
C	0.24426093467943	6.98073567763807	0.04688345939531
H	0.06620247406729	7.75943823554454	0.77527760091983
C	0.04920005685178	3.19450050396462	-0.10367306727449
C	-1.22845601720088	2.84816671858463	0.28504153543276
C	0.04428021061494	5.65396231978586	0.41008297927251
H	-0.28551349750369	5.42292099324022	1.41623099610141
C	0.26952834241147	4.61805580115214	-0.48372147088253
C	-3.47779313668825	-2.06596056643681	0.70766580599378
H	-4.51756826508528	-2.37389589389891	0.68023926997069
C	-3.83458611507305	0.46795594713277	0.76589927820902
C	-5.31423373549857	0.52056372607392	0.69544578488664
C	-8.11107817933636	0.63748007902878	0.57403866820423
C	-2.46021447118873	-2.94886870927525	0.62188657226809
H	-2.65792718366048	-4.00934548701562	0.51328721462209
C	-7.40003929911304	-0.06907410903685	-0.38777841896379
H	-7.90556437830143	-0.57382073413156	-1.19927164769724
C	0.60699257751739	9.61904091367040	-0.85199285685023
H	0.82691296704727	10.51738568356217	-1.42405392543720
H	-0.44549446894550	9.63157599909011	-0.55191827643060
H	1.23758902725469	9.59914337348062	0.04231398302513
C	0.72496338809605	4.93575140400566	-1.76714573998855
H	0.91765796765427	4.13648521756976	-2.47367766463311
C	-7.42224188038037	1.29035193080752	1.59594327890529
H	-7.99049520585503	1.83590702270807	2.33870457537407
C	0.91241876566814	6.24565867829704	-2.14590313194221
H	1.24453396333386	6.49778740514506	-3.14490433550446
C	-6.04648535712544	1.23055706802161	1.65040595171455
H	-5.52287612826371	1.73685608137680	2.45386365804014
C	-10.20504972833181	0.11413381406920	-0.40897434088426
H	-9.94718480627564	0.49742812323747	-1.40115867719123
H	-10.05573359341535	-0.97007775368423	-0.39021674652848
H	-11.24956638149380	0.33478196417516	-0.20105285413412
Rh	-1.18055404181151	-0.43644097379886	0.95284031441365
Cl	-0.99636321130741	-0.19898584227120	-1.39989223585536
O	-1.50640888756833	-0.99953502472663	3.86967978821348
C	-1.37802586647763	-0.76841289988626	2.77036528409668
Pt	1.33424086105844	0.36329066582868	-0.46414430648501
Cl	1.83351421873262	0.55760701015283	-2.70811586263873

Table S6. Cartesian coordinates of DFT (ωB97-D3/def2-TZVP) optimized transition states **[5]**‡ and **[5-Cl$_2$]**‡.

Coordinates for [**5**]‡

O	-6.54076647172076	6.51867659266585	0.01791560226223
O	-6.42178500828242	-6.57778880519167	-0.39869474856472
N	-2.17838894754030	-0.00017176863059	0.16687471689032
C	-4.46269253026173	-3.81736385600776	1.02923302586451
H	-4.35617929320691	-3.26347772910674	1.95527183315326
C	1.28157151316613	-2.71898884196119	0.03300194347804
C	-4.38620355590919	0.70865141448844	0.09925050932707
H	-5.23379961639038	1.37501272242720	0.10092433716597
C	-1.28232804599697	-2.71910142486756	0.03240577245938
C	-5.61333687795088	5.53308562771367	-0.00396590762262
C	-3.00794779807255	-1.05798482470276	0.08556579153583
C	-4.38875740918194	-0.63312408230297	0.03996811417616
H	-5.23450292896321	-1.29798751901328	-0.03082324970396
C	-5.30709143592465	4.76474451317382	-1.12084496152894
H	-5.80539609578083	4.92523663153031	-2.06664427630816
C	-2.63657627461353	2.46122619367929	0.24300670851852
C	-3.00667724349901	1.13543971302954	0.17135743996481
C	-4.34089454982206	3.77182433105329	-1.02555220480491
H	-4.09759279572549	3.17870156460085	-1.89937949857434
C	-3.67359044302791	3.52586289170667	0.16461232360520
C	-0.67606779482239	-4.03153426019948	0.00747358768951
H	-1.27379072553440	-4.93654285621944	0.00228156297249
C	-2.61431857381542	-2.43372979808634	0.03477745546451
C	-3.64899392510084	-3.50202655283624	-0.04922439579992
C	-5.54226957770816	-5.56224405041258	-0.22094128806874
C	0.67540344576999	-4.03147581578054	0.00781753527518
H	1.27319205830368	-4.93644386204793	0.00291108506331
C	-5.40691196317570	-4.83447582254115	0.95541493221980
H	-6.01772743211576	-5.05129919713390	1.82071866236393
C	-7.26011201524440	6.78412091047589	-1.16478508742520
C	-3.98027018686451	4.31574664739741	1.27275304614151
H	-3.46598683067944	4.14122973158924	2.21085749351408
C	-4.73414801657714	-5.25597212241596	-1.31381795742590
H	-4.85386823497991	-5.82753242850823	-2.22555490333386
C	-4.93926436439709	5.30360728607637	1.19456682543031
H	-5.18969917861427	5.91173139567531	2.05455739767490
C	-3.80527973780957	-4.24009958942556	-1.22386763828447
H	-3.18359553607784	-4.00463733632001	-2.08003705475172
C	-7.28522579250439	-6.90490526832269	0.66488375643144
O	6.42102746969805	-6.57836058721193	-0.39254053635189
O	6.54234689803256	6.51785347951795	0.00989222484348
N	2.17861364502877	0.00012990507042	0.16715044250936
C	4.34205791130764	3.76944085025933	-1.02845064018044
H	4.09850073650809	3.17489140639852	-1.90123384068379
C	-1.27820906489646	2.83899574544468	0.34018121097099
C	4.38868373228678	-0.63387860761567	0.04076061681329
H	5.23413360632215	-1.29917608284460	-0.02948125891589
C	1.27942837728341	2.83914493387716	0.34004828871413
C	5.54140702349682	-5.56270308039223	-0.21594690796679
C	3.00742010434213	1.13534868414153	0.17104608744204
C	4.38675459086015	0.70793511863873	0.09913934604690
H	5.23465878105149	1.37390577479934	0.10047739768696
C	5.40450078024493	-4.83502599319864	0.96028269824820
H	6.01408939609770	-5.05197973704448	1.82641757675192
C	2.61359589120644	-2.43375170318055	0.03609740274891
C	3.00765816471986	-1.05810854090561	0.08644888905216
C	4.46032776354215	-3.81779069524611	1.03286438206557
H	4.35261523691034	-3.26393972275709	1.95878482523414
C	3.64817607356384	-3.50224724995399	-0.04669523180771
C	0.70924351791922	4.08392188882359	0.36865053645628
H	1.29736944664343	4.99530911914005	0.35012884072395
C	2.63772862293104	2.46125859353509	0.24228287561418
C	3.67488150747151	3.52561509416299	0.16223940385798
C	5.61483484718293	5.53230373930652	-0.01010787491839
C	-0.70814381162655	4.08383873339337	0.36879870927623
H	-1.29638412799882	4.99515745131435	0.35048891588289
C	5.30835942098560	4.76206752454283	-1.12561332873489
H	5.80651901674235	4.92088864707384	-2.07177072892525
C	7.28259358427578	-6.90594332715775	0.67242213240945
C	3.80600151029109	-4.24022411242139	-1.22118216898332
H	3.18552972423121	-4.00461422739930	-2.07819094011926
C	4.94093555286396	5.30496303086173	1.18893120652368
H	5.19159725510311	5.91451731847125	2.04784287645583
C	4.73486405562058	-5.25620907511056	-1.30992836076644
H	4.85578861216652	-5.82771205842701	-2.22154163017324
C	3.98181836165013	4.31735566538732	1.26898334773042
H	3.46770875798682	4.14451506546927	2.20749328268671
Cl	0.00063301148014	1.49292021031494	-2.03984012601172
O	-0.00517308730771	1.29430035241886	3.29027158935487
C	-0.00135108091808	1.30188285032261	2.16017222436450
H	-7.94150200054421	7.59810645852005	-0.92846638219666
H	-6.59580950454354	7.09521223607144	-1.97684309137269
H	-7.83885186125993	5.91192318370567	-1.48452643382183
H	-7.90430865343281	-7.72688631094472	0.31270152280368
H	-6.72875657554683	-7.22925626008463	1.54984595005903
H	-7.92811474857190	-6.06018806262187	0.93216541620713
H	6.72452840546533	-7.23005986767015	1.55646610509670
H	7.90186709795364	-7.72819688653660	0.32121488777299
H	7.92544047116573	-6.06153590163360	0.94078743444071
C	7.26160601018307	6.78114153644834	-1.17333547568496
H	7.94304363183196	7.59552042821655	-0.93850897521228
H	7.84030080819671	5.90835502348854	-1.49155044362549
H	6.59726192423152	7.09079833352798	-1.98590634599171
Pt	-0.00047342926261	-1.27599812500039	0.06953940774582
Rh	0.00072879948494	1.37316847744544	0.28252938140875

Coordinates for [**5-Cl$_2$**]‡

O	6.40258527780037	6.48521421555624	-0.43447677139281
O	6.54958678958154	-6.60847492202437	-0.05266103465828
N	2.17275046671390	-0.10938907727519	0.15332623479678
C	4.33983090908038	-3.85060451638915	-1.03890707658531
H	4.08983883735820	-3.24377695620509	-1.90128972889937
C	-1.28238650466517	-2.94789255542758	0.39517106745368
C	4.37457943785743	0.53414181428535	0.00267171670921
H	5.21564647984082	1.20409995020122	-0.07308163591238
C	1.28037727915239	-2.94795195532498	0.39540320127159
C	5.53300729259951	5.46499127098863	-0.24554072301629
C	3.00661318271272	-1.24356983238120	0.14975031566603
C	4.38124394612981	-0.80910820176033	0.05772510227944
H	5.23439837515426	-1.46794221763391	0.05285124517064
C	5.40558808639121	4.74875062818284	0.93950010375103
H	6.01652031055943	4.97991144550231	1.80088402457477
C	2.61196383931098	2.34290501146905	0.04824829377614
C	2.99310465745019	0.94835569431014	0.06926172735297
C	4.46714001359449	3.72794814153268	1.02768928044099
H	4.36055121395092	3.18490026819246	1.95994950050911
C	3.65542924483851	3.40216600932668	-0.04811792421255
C	0.70958186814265	-4.19010111291298	0.47183043848141
H	1.29385305305562	-5.10387267938784	0.47465071190172
C	2.63904008173375	-2.56931820786244	0.25456249025920
C	3.67570081130473	-3.62982347745319	0.15846028034417
C	5.61952035704666	-5.62631736549873	-0.05293203752734
C	-0.71167449740908	-4.19006357347250	0.47169458764705
H	-1.29600740709196	-5.10379608427817	0.47441698028698
C	5.30748937131428	-4.83890211965706	-1.15511745973148
H	5.80224603234562	-4.98165985255371	-2.10553616528730
C	7.26518279790061	6.83365101531383	0.62384982072441

C	3.80045435830935	4.12514435718648	-1.23291113864599
H	3.17221792019259	3.87678875322564	-2.08089999333853
C	4.94857182632250	-5.42121677231073	1.15201450269762
H	5.20464564042589	-6.04310289496470	2.00033737205053
C	4.72504241336938	5.14340088379737	-1.33482542137100
H	4.83888851907617	5.70767563075025	-2.25173480273069
C	3.98633553115043	-4.43863413371738	1.25177924406561
H	3.47649895850049	-4.28125949728914	2.19532693270795
C	7.27183189253962	-6.84460390999773	-1.24021537492323
O	-6.55247871671426	-6.60715599429187	-0.05304431572232
O	-6.39900162933318	6.48774168999698	-0.43375944741017
N	-2.17315798522008	-0.10953112259110	0.15297416711706
C	-4.46504633833154	3.72904591915353	1.02767359912964
H	-4.35862387623137	3.18581401949839	1.95984596078582
C	1.31233770932598	2.69775583659573	0.07695642037787
C	-4.38215051631560	-0.80764870027745	0.05692940649333
H	-5.23579273077581	-1.46585317437754	0.05186383466851
C	-1.31093052326242	2.69767750515970	0.07674401497961
C	-5.62224759449473	-5.62515639039226	-0.05331518234280
C	-2.99265084525863	0.94883957257623	0.06879420704151
C	-4.37445081780807	0.53559787609690	0.00189790720197
H	-5.21500531709827	1.20617865557895	-0.07403069249670
C	-5.31036601174392	-4.83752004083183	-1.15538439382288
H	-5.80540526908480	-4.97994966558023	-2.10570510126019
C	-2.64094696732952	-2.56897318566301	0.25413941095859
C	-3.00785983704267	-1.24307032264015	0.14923119904511
C	-4.34245904373962	-3.84946116741559	-1.03919635194722
H	-4.09254769592644	-3.24250559060088	-1.90151154005222
C	-3.67792818747447	-3.62913490621458	0.15803576027738
C	-0.67503355872932	3.98505094414402	0.09425814944553
H	-1.26941137080055	4.89036562402847	0.11341771310522
C	-2.61067544190035	2.34318682398758	0.04791089796539
C	-3.65368281007628	3.40293839915324	-0.04829622084218
C	-5.53006324815941	5.46691405838825	-0.24513339530630
C	0.67642359299718	3.98508645554075	0.09435867830241
H	1.27079854832112	4.89040187071548	0.11360539130372
C	-5.40290529253098	4.75041253268526	0.93977759617252
H	-6.01357046083778	4.98180302337885	1.80128863358039
C	-7.27508323946076	-6.84286761793647	-1.24046210308383
C	-3.98847065489953	-4.43813493122433	1.25124957646927
H	-3.47835864388816	-4.28109890308884	2.19470446257022
C	-4.72248905919470	5.14496689056130	-1.33460242126906
H	-4.83613306666803	5.70944748226467	-2.25141037893832
C	-4.95094772200686	-5.42047931110743	1.15150782663887
H	-5.20693321131794	-6.04251177809310	1.99974971154837
C	-3.79849153286093	4.12614218336198	-1.23297584101191
H	-3.17052131631602	3.87755271795135	-2.08109377763443
Cl	0.00051595404655	1.36163436788921	2.42061139592831
H	7.87465648557941	7.65759551743191	0.25991613628057
H	6.70699599105475	7.16310642264437	1.50568266488451
H	7.91706229892665	5.99869940397592	0.89922060942188
H	7.95806987989690	-7.65888575704277	-1.01981576462247
H	6.61030871007082	-7.14276200927933	-2.05923654923344
H	7.84534707205036	-5.96220158925589	-1.54062050449549
H	-6.61383414747358	-7.14092820683461	-2.05974041526138
H	-7.96139502851900	-7.65709223109528	-1.02008058608081
H	-7.84853891652903	-5.96029853486083	-1.54049041311610
C	-7.26092416040381	6.83681560657723	0.62491070335957
H	-7.86973643940101	7.66139881278721	0.26131658031035
H	-7.91350278697917	6.00243617864088	0.90036292357807
H	-6.70212361938327	7.16558809219016	1.50661035661920
C	-0.00118403039891	-1.52391500943396	2.21097354520358
O	-0.00138366397068	-1.77284028833021	3.31223222400109
Cl	-0.00073824605964	-1.89105382359364	-1.98762625173077
Cl	0.00094135396554	1.42135703075451	-2.20618316125624
Pt	0.00076053399510	1.25965342817059	0.09350649373616
Rh	-0.00096222192044	-1.49806186386950	0.30774176374916

Table S7. Cartesian coordinates of DFT optimized (b3pw91/6-31G(d,p) and SDD for Pt, Rh, Te) geometries of **4-Rh(CO)$_2$Cl**.

Coordinates for **4**-Rh(CO)$_2$Cl-**1**

O	3.4299850	13.4395420	4.8448480
O	8.6571360	4.4275560	13.1444240
N	2.4013890	8.1343850	10.3505490
C	5.2510450	4.5549680	11.7365690
H	4.5339660	3.9159420	11.2293090
C	-0.2710550	5.1289440	12.1024170
C	4.0063120	9.0748640	9.0404360
H	4.4537200	9.6591050	8.2486070
C	2.4125300	5.8987680	11.8927210
C	2.9905660	12.5437640	5.7665350
C	3.5997300	7.6159320	10.7002350
C	4.6389530	8.2278480	9.9034790
H	5.6945290	7.9979660	9.9530600
C	2.9710320	12.7654040	7.1468060
H	3.3149420	13.7032510	7.5685920
C	1.5518430	9.4840180	8.4510340
C	2.5733340	8.9616260	9.2919100
C	2.5002720	11.7660380	7.9990300
H	2.4852650	11.9468580	9.0703480
C	2.0306960	10.5428640	7.5090180
C	2.0790000	4.7143760	12.5524820
H	2.8614060	4.0725100	12.9476580
C	3.6394940	6.4802270	11.5513320
C	4.9376390	5.9009090	11.9586180
C	7.4321940	4.8401110	12.7329570
C	0.7382840	4.3119730	12.6297700
H	0.5018020	3.3308530	13.0332090
C	6.4817870	4.0211820	12.1143520
H	6.6903530	2.9765940	11.9123310
C	3.9051820	14.6875850	5.3062770
H	4.2048330	15.2445880	4.4172200
H	4.7738280	14.5719450	5.9675480
H	3.1242120	15.2488880	5.8356180
C	2.0614090	10.3400750	6.1179110
H	1.7189620	9.3917840	5.7125630
C	7.1359290	6.1916870	12.9574300
H	7.8822400	6.8122640	13.4431780
C	2.5345840	11.3194040	5.2582670
H	2.5672370	11.1593880	4.1850450
C	5.9104350	6.7104740	12.5729080
H	5.6860040	7.7556260	12.7663090

C	9.0020300	3.0700800	12.9538810
H	9.0112310	2.7994120	11.8900750
H	8.3181740	2.3994430	13.4899320
H	10.0078170	2.9543990	13.3602610
O	-3.3948860	0.4746180	15.1911290
O	-8.3270340	8.6208010	5.6228290
N	-2.3194760	6.2960940	10.0932910
C	-5.2616500	9.1841640	7.5947700
H	-4.7110400	9.9902110	8.0709840
C	0.2042000	9.0293050	8.3995710
C	-3.9878270	5.1245850	11.1123770
H	-4.4784740	4.4784840	11.8260580
C	-2.3145860	8.1876480	8.2217520
C	-3.0002900	1.4620890	14.3484620
C	-3.5212290	6.5896460	9.4845410
C	-4.5749110	5.8574080	10.1216790
H	-5.6251140	5.9200910	9.8737150
C	-3.1599190	1.4326170	12.9590790
H	-3.6141840	0.5809970	12.4651020
C	-1.6229020	4.7728820	11.9670780
C	-2.5625690	5.3955510	11.0923780
C	-2.7198210	2.5111660	12.1928110
H	-2.8358570	2.4752570	11.1130280
C	-2.1116280	3.6267090	12.7805340
C	-1.9860950	9.2620290	7.3784190
H	-2.6990970	9.7357510	6.7066830
C	-3.5524740	7.5607830	8.4535430
C	-4.7977580	7.8689530	7.7225640
C	-7.1746860	8.4484300	6.3180720
C	-0.6748390	9.7080120	7.4920560
H	-0.3427000	10.5679950	6.9153150
C	-6.4352570	9.4808880	6.9041190
H	-6.7662950	10.5114010	6.8409220
C	-4.0214390	-0.6641720	14.6368030
H	-4.2595150	-1.3172860	15.4776590
H	-4.9489720	-0.4014650	14.1117220
H	-3.3560790	-1.1972200	13.9451910
C	-1.9469220	3.6321340	14.1789620
H	-1.4780790	4.4908080	14.6528890
C	-6.7263750	7.1255240	6.4381710
H	-7.3084450	6.3370540	5.9715010
C	-2.3906620	2.5719300	14.9516500
H	-2.2800030	2.5799490	16.0313940
C	-5.5601410	6.8445370	7.1307380
H	-5.2140990	5.8170560	7.2011710
C	-8.8204340	9.9362560	5.4671200
H	-9.0569510	10.3977350	6.4345850
H	-8.1084350	10.5749480	4.9286110
H	-9.7359340	9.8477830	4.8804200
Rh	0.3661160	8.6657800	13.5387010
Te	0.6343930	6.9505660	11.4296370
Pt	-0.8245210	7.5617950	9.3560440
C	0.1538750	9.7890590	15.0048630
O	0.0226450	10.4713890	15.9180700
Cl	0.3092220	6.8816550	15.0657650
C	0.4394310	10.0942320	12.3639740
O	0.4892760	11.0181960	11.6768990

Coordinates for **4**-$Rh(CO)_2Cl$-**2**

O	3.3973320	13.5465910	4.9892630
O	8.6448440	4.3261050	13.1139440
N	2.4112560	8.0635130	10.3129780
C	5.2262720	4.4807150	11.7384900
H	4.4932830	3.8434210	11.2521520
C	-0.2827420	5.1729670	12.1676640
C	4.0060850	9.0348460	9.0199440
H	4.4492210	9.6358360	8.2382970
C	2.4106350	5.8815910	11.8987530
C	2.9635620	12.6126680	5.8756190
C	3.6094660	7.5498760	10.6581170
C	4.6442780	8.1739330	9.8654860
H	5.7012770	7.9496630	9.9099330
C	2.9180350	12.7904650	7.2616340
H	3.2337530	13.7219820	7.7180030
C	1.5502270	9.4488540	8.4465300
C	2.5738300	8.9145460	9.2735800
C	2.4567990	11.7554410	8.0753790
H	2.4177990	11.9003390	9.1515850
C	2.0216660	10.5391750	7.5380990
C	2.0654190	4.7191830	12.5955220
H	2.8419100	4.0693490	12.9902660
C	3.6440920	6.4274260	11.5286960
C	4.9374190	5.8361320	11.9344690
C	7.4224060	4.7502640	12.7061420
C	0.7199460	4.3468830	12.7034930
H	0.4724120	3.3780960	13.1305010
C	6.4519900	3.9343930	12.1153330
H	6.6412260	2.8824410	11.9333600
C	3.8333620	14.7908260	5.4972340
H	4.1327750	15.3829610	4.6310260
H	4.6941090	14.6761860	6.1689450
H	3.0302620	15.3154550	6.0309940
C	2.0770550	10.3797610	6.1425480
H	1.7611090	9.4378080	5.7021830
C	7.1508680	6.1110830	12.9044730
H	7.9131200	6.7297210	13.3674820
C	2.5425440	11.3956770	5.3216270
H	2.5949680	11.2707670	4.2445190
C	5.9300580	6.6421620	12.5212760
H	5.7260420	7.6954720	12.6922840

C	8.9682090	2.9610190	12.9415020
H	8.9603830	2.6730520	11.8822550
H	8.2817120	2.3087400	13.4966320
H	9.9772040	2.8375050	13.3375110
O	-3.4224290	0.4453530	15.1606110
O	-8.3207230	8.5504040	5.6016700
N	-2.3258180	6.3003270	10.1267360
C	-5.2560570	9.1384270	7.5676600
H	-4.7050540	9.9502850	8.0333720
C	0.2037220	8.9881710	8.3880160
C	-3.9982650	5.1508860	11.1636270
H	-4.4917750	4.5181190	11.8873750
C	-2.3094860	8.1428980	8.2095760
C	-3.0223060	1.4502290	14.3419460
C	-3.5256850	6.5812470	9.5070250
C	-4.5822550	5.8643630	10.1572570
H	-5.6316440	5.9227900	9.9048100
C	-3.1527910	1.4433430	12.9494870
H	-3.5881170	0.5958600	12.4319230
C	-1.6330790	4.8124620	12.0283830
C	-2.5725570	5.4218700	11.1423710
C	-2.7090340	2.5390260	12.2101250
H	-2.8042560	2.5198850	11.1280330
C	-2.1257130	3.6533740	12.8252820
C	-1.9807680	9.2092100	7.3566760
H	-2.6938380	9.6792190	6.6825190
C	-3.5513020	7.5260210	8.4531650
C	-4.7947120	7.8243060	7.7151100
C	-7.1691750	8.3864430	6.3004380
C	-0.6712180	9.6605630	7.4732580
H	-0.3401140	10.5208000	6.8965690
C	-6.4287180	9.4263790	6.8718130
H	-6.7581630	10.4563460	6.7934420
C	-4.0244090	-0.6916180	14.5750580
H	-4.2716400	-1.3609860	15.4002680
H	-4.9440840	-0.4306190	14.0356920
H	-3.3387710	-1.2052920	13.8887620
C	-1.9924380	3.6338080	14.2257820
H	-1.5425530	4.4849580	14.7285300
C	-6.7233300	7.0646920	6.4406640
H	-7.3064050	6.2703470	5.9853340
C	-2.4378910	2.5570060	14.9744870
H	-2.3488660	2.5488260	16.0562210
C	-5.5581900	6.7921920	7.1385690
H	-5.2139090	5.7653290	7.2251560
C	-8.8112460	9.8644170	5.4256420
H	-9.0478310	10.3409070	6.3857730
H	-8.0973330	10.4934890	4.8784550
H	-9.7262860	9.7689950	4.8392860
Rh	0.4519090	8.7063630	13.5455940
Te	0.6525920	6.9811360	11.4392740
Pt	-0.8255930	7.5393640	9.3616680
C	0.5951210	7.3182350	14.7559290
O	0.6754150	6.4825010	15.5482030
C	0.2868490	9.9747000	14.8960210
Cl	0.2620190	10.4799790	12.0258190
O	0.1850980	10.7662510	15.7205040

Coordinates for **4**-$Rh(CO)_2Cl$-**3**

O	3.4902860	13.2326690	4.9336770
O	8.5427320	4.1232460	12.9608590
N	2.4255110	8.4734470	10.8792280
C	5.0616110	4.5563330	11.8252610
H	4.2749190	4.0049350	11.3180470
C	-0.2696610	5.0853450	12.4137020
C	3.9310680	8.8563140	9.1840300
H	4.3209100	9.1992810	8.2361620
C	2.3340890	6.0322080	12.3179240
C	3.0498290	12.4098680	5.9180300
C	3.5630190	7.7239850	11.0916930
C	4.5310780	8.0075910	10.0748650
H	5.4980300	7.5318780	9.9882060
C	3.2597930	12.6192230	7.2849960
H	3.8040010	13.4860960	7.6425780
C	1.5471770	9.6003730	8.8227610
C	2.5838970	9.0711500	9.6429430
C	2.7633220	11.6992640	8.2065760
H	2.9322610	11.8668560	9.2672280
C	2.0372310	10.5700240	7.8036090
C	2.0770600	4.7846920	12.9157810
H	2.9017000	4.1746330	13.2727520
C	3.5615520	6.5837710	11.9276670
C	4.8462410	5.8909730	12.1886100
C	7.3186280	4.6364410	12.6782780
C	0.7733890	4.2947060	12.9377740
H	0.5809240	3.2774550	13.2678560
C	6.2824310	3.9266050	12.0618740
H	6.4163030	2.8961590	11.7522680
C	4.2233290	14.3831380	5.3058800
H	4.4798530	14.8914620	4.3752700
H	5.1460170	14.1205240	5.8389640
H	3.6265200	15.0586470	5.9320680
C	1.8457660	10.3754460	6.4222010
H	1.3170690	9.4904740	6.0792440
C	7.1202070	5.9768650	13.0369300
H	7.9361520	6.5132800	13.5109540
C	2.3430130	11.2750390	5.4935560
H	2.2072460	11.1180670	4.4280630
C	5.9055140	6.5957250	12.7898070
H	5.7525070	7.6336280	13.0720820

C	8.7953230	2.7753870	12.6208240
H	8.7156290	2.6076920	11.5387950
H	8.1129160	2.0908950	13.1413510
H	9.8185170	2.5701700	12.9390860
O	-3.2077240	-0.0746060	14.8488440
O	-8.2330990	8.6131810	5.8733200
N	-2.2685160	6.2651990	10.3890050
C	-5.2697290	9.1643280	7.9989170
H	-4.7805880	9.9539530	8.5620370
C	0.1951260	9.1604270	8.8370470
C	-3.9165600	4.9318480	11.2383020
H	-4.3991670	4.2053440	11.8763360
C	-2.2820370	8.2474350	8.6173110
C	-2.8405770	1.0192470	14.1364330
C	-3.4600050	6.5391490	9.7502410
C	-4.5003640	5.7112610	10.2831290
H	-5.5402430	5.7404610	9.9896180
C	-2.9121320	1.1242870	12.7435410
H	-3.2691360	0.2991400	12.1375480
C	-1.5819260	4.6470170	12.1805310
C	-2.5098190	5.2781060	11.3041790
C	-2.5096560	2.3042770	12.1193650
H	-2.5569910	2.3725140	11.0361110
C	-2.0267290	3.3952170	12.8521000
C	-2.0032080	9.3883620	7.8460730
H	-2.7408840	9.8752990	7.2120960
C	-3.5010240	7.5652350	8.7802450
C	-4.7368580	7.8697820	8.0298540
C	-7.0959120	8.4423120	6.5934520
C	-0.7110420	9.8721140	7.9835180
H	-0.4104820	10.7834550	7.4721540
C	-6.4354180	9.4573590	7.2931490
H	-6.8216680	10.4703630	7.3062350
C	-3.7077590	-1.1931520	14.1434550
H	-3.9438460	-1.9447380	14.8980490
H	-4.6195470	-0.9451620	13.5849980
H	-2.9612610	-1.6018530	13.4502730
C	-1.9527290	3.2640140	14.2509950
H	-1.5853060	4.0978280	14.8426540
C	-6.5776860	7.1398950	6.6159850
H	-7.0990390	6.3654190	6.0622180
C	-2.3573610	2.1017220	14.8860720
H	-2.3148690	2.0060000	15.9664200
C	-5.4201320	6.8619580	7.3245310
H	-5.0192980	5.8520960	7.3198440
C	-8.7942890	9.9092030	5.8123540
H	-9.0876500	10.2711470	6.8062420
H	-8.1021550	10.6294090	5.3573060
H	-9.6838100	9.8238100	5.1865560
Rh	2.0802720	10.1377380	12.3249500
Te	0.5022810	7.0121840	11.9839230
O	1.9282380	12.3256800	14.3550850
C	1.9750500	11.4874250	13.5699260
Cl	4.3216680	9.9829300	13.0631840
Pt	-0.7887910	7.6252930	9.7464400
C	0.3278530	10.4932660	11.8213030
O	-0.7469330	10.8459950	11.6022630

Coordinates for **4**-$Rh(CO)_2Cl$-**4**

O	3.4704080	13.3495260	4.9354270
O	8.4803450	3.9261730	12.5427050
N	2.4472740	8.6006620	10.8884120
C	4.9734300	4.6043540	11.6257550
H	4.1306950	4.1229930	11.1380100
C	-0.2577580	5.2379170	12.4475770
C	3.9517580	9.0367040	9.2075330
H	4.3368750	9.4024460	8.2660860
C	2.3491230	6.1589410	12.2976410
C	3.0269550	12.5204490	5.9146740
C	3.5956260	7.8482310	11.0808920
C	4.5642590	8.1748780	10.0772070
H	5.5369350	7.7134340	9.9762750
C	3.0980520	12.7956800	7.2840870
H	3.5194900	13.7261940	7.6475760
C	1.5588270	9.6796100	8.8055230
C	2.5928110	9.2108820	9.6585190
C	2.6160730	11.8622950	8.2003840
H	2.6611870	12.0837270	9.2630690
C	2.0395470	10.6552470	7.7853420
C	2.0928020	4.9198950	12.9111420
H	2.9178100	4.3030910	13.2562600
C	3.5826750	6.6855090	11.8845420
C	4.8473970	5.9276250	12.0667480
C	7.2734370	4.5168040	12.3547930
C	0.7841440	4.4451320	12.9667490
H	0.5876450	3.4337230	13.3128770
C	6.1671130	3.8982150	11.7631540
H	6.2250230	2.8796750	11.3959720
C	4.0457480	14.5824150	5.3184390
H	4.3296190	15.0839900	4.3919980
H	4.9404190	14.4374900	5.9377110
H	3.3304750	15.2116970	5.8635460
C	1.9795510	10.3976840	6.4031450
H	1.5591030	9.4578470	6.0558540
C	7.1674560	5.8439790	12.7917180
H	8.0347020	6.3104620	13.2482890
C	2.4677280	11.3096620	5.4809680
H	2.4338890	11.1069940	4.4150380
C	5.9757860	6.5361730	12.6445560
H	5.9085170	7.5598700	12.9977200

C	8.6395610	2.5868160	12.1204330
H	8.4926250	2.4826440	11.0375800
H	7.9493130	1.9121930	12.6433050
H	9.6654530	2.3116580	12.3694960
O	-3.2085410	0.2020420	15.1182560
O	-8.1179990	8.4056990	5.6211420
N	-2.2390470	6.3250710	10.3709820
C	-5.1963950	9.0816890	7.7688200
H	-4.7195430	9.9023950	8.2968660
C	0.2245070	9.1828720	8.7727410
C	-3.9044100	5.0451660	11.2707960
H	-4.3983490	4.3568340	11.9417050
C	-2.2207450	8.2086180	8.5013610
C	-2.8406680	1.2626500	14.3571270
C	-3.4195640	6.5638670	9.7003520
C	-4.4711930	5.7698200	10.2643110
H	-5.5066400	5.7859790	9.9544700
C	-2.9291400	1.3114440	12.9621550
H	-3.3009580	0.4655820	12.3948520
C	-1.5745550	4.7962380	12.2404040
C	-2.4967340	5.3904490	11.3352560
C	-2.5243680	2.4611950	12.2852800
H	-2.5843160	2.4852700	11.2008120
C	-2.0225250	3.5769030	12.9664930
C	-1.9325790	9.3131730	7.6811590
H	-2.6554400	9.7555530	6.9992220
C	-3.4422060	7.5325930	8.6731250
C	-4.6627230	7.7920010	7.8822170
C	-6.9943740	8.2777740	6.3714070
C	-0.6586910	9.8319400	7.8467580
H	-0.3612550	10.7322050	7.3155470
C	-6.3486690	9.3318900	7.0255710
H	-6.7363150	10.3431700	6.9748180
C	-3.7301260	-0.9381630	14.4653620
H	-3.9644070	-1.6559710	15.2527370
H	-4.6464710	-0.7025370	13.9089940
H	-2.9975420	-1.3831930	13.7796820
C	-1.9308500	3.5014200	14.3686060
H	-1.5482000	4.3551990	14.9207660
C	-6.4754370	6.9797730	6.4768920
H	-6.9854000	6.1742870	5.9578100
C	-2.3376790	2.3699430	15.0557120
H	-2.2820840	2.3179150	16.1384630
C	-5.3313730	6.7446280	7.2220090
H	-4.9295350	5.7369320	7.2823000
C	-8.6791310	9.6951270	5.4778660
H	-8.9914370	10.1111410	6.4444550
H	-7.9792720	10.3904950	4.9967100
H	-9.5566720	9.5734670	4.8411800
Rh	2.0333850	10.0664900	12.5375530
Te	0.5191440	7.1621910	11.9797890
O	1.3686750	12.0550930	14.6678270
C	1.6286260	11.2898720	13.8506500
Cl	0.1440200	10.9930770	11.4751150
Pt	-0.7542280	7.6657120	9.7011270
C	3.5326900	9.5318800	13.4756420
O	4.4581710	9.2934300	14.1235560

Coordinates for **4**-$Rh(CO)_2Cl$-**5**

O	3.4307220	13.3523680	4.7736840
O	8.6455430	4.4412260	13.2107590
N	2.4047270	8.1215380	10.3536740
C	5.2415950	4.5579910	11.7975080
H	4.5231270	3.9140470	11.2983280
C	-0.2777290	5.1610820	12.1755160
C	4.0129630	9.0383140	9.0290720
H	4.4623540	9.6108840	8.2299500
C	2.4073920	5.9241030	11.9467570
C	2.9952680	12.4729110	5.7117790
C	3.5997870	7.6039370	10.7083110
C	4.6418310	8.1979490	9.9009590
H	5.6962890	7.9636350	9.9528160
C	3.0118250	12.7053100	7.0904710
H	3.3829580	13.6394440	7.4969740
C	1.5571980	9.4641950	8.4517970
C	2.5798960	8.9385510	9.2871630
C	2.5415510	11.7221780	7.9612180
H	2.5544060	11.9123450	9.0309020
C	2.0361900	10.5050330	7.4913820
C	2.0743160	4.7490770	12.6293740
H	2.8576850	4.1091760	13.0267530
C	3.6356040	6.4856410	11.5847520
C	4.9324090	5.9079420	11.9997700
C	7.4225580	4.8511610	12.7921540
C	0.7347900	4.3490260	12.7152630
H	0.5000730	3.3715470	13.1292580
C	6.4704630	4.0260530	12.1842540
H	6.6765570	2.9782180	11.9970660
C	3.9399610	14.5952530	5.2136900
H	4.2293880	15.1390120	4.3132000
H	4.8212120	14.4681200	5.8557250
H	3.1818840	15.1752120	5.7557980
C	2.0303270	10.2910850	6.1014440
H	1.6601480	9.3468100	5.7114110
C	7.1299830	6.2068070	12.9970370
H	7.8776810	6.8322500	13.4742990
C	2.5035150	11.2539490	5.2237230
H	2.5086270	11.0851990	4.1513850
C	5.9067390	6.7239260	12.6032600
H	5.6855560	7.7726480	12.7808130

C	8.9889960	3.0810230	13.0368070
H	8.9982980	2.7976490	11.9763600
H	8.3041880	2.4177600	13.5807590
H	9.9944350	2.9692620	13.4450140
O	-3.3802560	0.3051810	14.9982200
O	-8.3483680	8.6667270	5.7147510
N	-2.3263050	6.3236410	10.1561700
C	-5.2736540	9.2149170	7.6751870
H	-4.7201050	10.0174020	8.1539930
C	0.2009900	9.0275220	8.4260430
C	-3.9871310	5.1302770	11.1610910
H	-4.4731140	4.4722480	11.8671020
C	-2.3248520	8.2077690	8.2790040
C	-2.9861380	1.3394770	14.2150420
C	-3.5308420	6.6146500	9.5485740
C	-4.5799110	5.8713460	10.1802700
H	-5.6306760	5.9307150	9.9341090
C	-3.0972670	1.3708220	12.8210610
H	-3.5115440	0.5318990	12.2732350
C	-1.6209720	4.7867330	12.0167220
C	-2.5636170	5.4125170	11.1445290
C	-2.6618270	2.4945180	12.1201130
H	-2.7423170	2.5055380	11.0366590
C	-2.1050220	3.5993020	12.7758430
C	-1.9994190	9.2796830	7.4333740
H	-2.7170600	9.7599060	6.7714430
C	-3.5650330	7.5851420	8.5191700
C	-4.8120730	7.8979270	7.7939180
C	-7.1936730	8.4888470	6.4034420
C	-0.6819530	9.7145250	7.5305960
H	-0.3491990	10.5713270	6.9496300
C	-6.4499770	9.5170480	6.9919650
H	-6.7800060	10.5482860	6.9366260
C	-3.9558370	-0.8242170	14.3723590
H	-4.2025550	-1.5207290	15.1748700
H	-4.8726480	-0.5625150	13.8285750
H	-3.2528260	-1.3067210	13.6810920
C	-1.9919780	3.5424970	14.1770630
H	-1.5679830	4.3871860	14.7119050
C	-6.7468550	7.1644230	6.5139860
H	-7.3322390	6.3796260	6.0453380
C	-2.4301190	2.4373250	14.8876940
H	-2.3579910	2.4003910	15.9700390
C	-5.5784380	6.8775990	7.2002230
H	-5.2337550	5.8491920	7.2633990
C	-8.8422410	9.9836960	5.5700120
H	-9.0734500	10.4386960	6.5417030
H	-8.1327560	10.6252720	5.0317780
H	-9.7607520	9.8990060	4.9875850
Rh	0.3338420	8.6626250	13.4639490
Te	0.6310960	6.9853800	11.4807540
Pt	-0.8315060	7.5777650	9.4053830
C	0.2929720	7.2961160	14.7965910
O	0.2870780	6.5257550	15.6456710
Cl	0.0167370	10.1958520	15.2119430
C	0.5003170	10.1897590	12.3063690
O	0.6218500	11.1431790	11.6853030

Coordinates for **4**-$Rh(CO)_2Cl$-**6**

O	3.4471250	13.0583160	4.6512430
O	8.5278170	4.2036120	12.8826690
N	2.4598240	8.6246290	10.8474980
C	5.0393900	4.6954990	11.7941200
H	4.2430980	4.1643860	11.2805810
C	-0.2481320	5.1637360	12.4354630
C	3.9245960	8.8582430	9.0999050
H	4.2906110	9.1241650	8.1182730
C	2.3261880	6.1885190	12.3663060
C	3.0232220	12.2904140	5.6852310
C	3.5717230	7.8465530	11.0770710
C	4.5241320	8.0427510	10.0211460
H	5.4656700	7.5191870	9.9300140
C	3.2835000	12.5556340	7.0338870
H	3.8547690	13.4268880	7.3337910
C	1.5547100	9.6505120	8.7605870
C	2.5988200	9.1448590	9.5849910
C	2.7991400	11.6889330	8.0114010
H	3.0042020	11.9035620	9.0567540
C	2.0346420	10.5602170	7.6847210
C	2.1004370	4.9250730	12.9481440
H	2.9406280	4.3296210	13.2932210
C	3.5524370	6.7299060	11.9496730
C	4.8352490	6.0209110	12.1961120
C	7.3059360	4.7329460	12.6263330
C	0.8119670	4.3993250	12.9634920
H	0.6457630	3.3754390	13.2880520
C	6.2571980	4.0497950	12.0013100
H	6.3787460	3.0271210	11.6623760
C	4.2071420	14.2137900	4.9466410
H	4.4392650	14.6756530	3.9859540
H	5.1436140	13.9619990	5.4606160
H	3.6400460	14.9252030	5.5603860
C	1.7932740	10.3087850	6.3199380
H	1.2340910	9.4220750	6.0349910
C	7.1212020	6.0643550	13.0234250
H	7.9451490	6.5814180	13.5048160
C	2.2789930	11.1537480	5.3359320
H	2.1042190	10.9526220	4.2836460
C	5.9080610	6.6968720	12.8043470
H	5.7777300	7.7260630	13.1237310

C	8.7662760	2.8620830	12.5062700	C	-0.7163920	9.9249790	7.9654910
H	8.6754590	2.7230550	11.4212010	H	-0.4215230	10.8307200	7.4412380
H	8.0828920	2.1708150	13.0160970	C	-6.4405350	9.4893590	7.3206130
H	9.7905000	2.6411370	12.8099150	H	-6.8346030	10.4993020	7.3342510
O	-3.1052400	-0.0749540	14.7985480	C	-3.5980480	-1.1876350	14.0788260
O	-8.2320330	8.6313230	5.9017460	H	-3.8216390	-1.9531940	14.8230810
N	-2.2515430	6.3363120	10.4221500	H	-4.5157890	-0.9404490	13.5299000
C	-5.2723030	9.2054400	8.0256470	H	-2.8516330	-1.5777160	13.3749050
H	-4.7891460	9.9989360	8.5885280	C	-1.8952590	3.2880150	14.2474910
C	0.1991260	9.2236550	8.8178010	H	-1.5374970	4.1178480	14.8505750
C	-3.8888490	4.9793380	11.2585470	C	-6.5653300	7.1706800	6.6433090
H	-4.3639140	4.2434680	11.8914670	H	-7.0810330	6.3923030	6.0897500
C	-2.2754850	8.3054930	8.6350360	C	-2.2821830	2.1109530	14.8659600
C	-2.7555680	1.0342450	14.1017050	H	-2.2340520	1.9993620	15.9445280
C	-3.4450470	6.6009250	9.7826750	C	-5.4056320	6.9014650	7.3516660
C	-4.4793080	5.7609670	10.3104310	H	-4.9972490	5.8946180	7.3470520
H	-5.5191500	5.7836260	10.0163470	C	-8.8049350	9.9226090	5.8431150
C	-2.8356680	1.1599480	12.7108760	H	-9.1000600	10.2804980	6.8378640
H	-3.1856860	0.3399170	12.0939660	H	-8.1198170	10.6493420	5.3879400
C	-1.5518520	4.7065160	12.1974540	H	-9.6944590	9.8298720	5.2184230
C	-2.4846980	5.3383370	11.3270800	Rh	1.6576450	9.7794370	12.4743780
C	-2.4510880	2.3543290	12.1032950	Te	0.4617200	7.1327350	12.0563910
H	-2.5043910	2.4386820	11.0214170	Pt	-0.7784470	7.7074250	9.7689370
C	-1.9781390	3.4396630	12.8509690	C	0.4744820	10.9052740	11.4526290
C	-2.0093840	9.4394380	7.8491870	O	-0.1674470	11.7360350	10.9915220
H	-2.7557180	9.9173520	7.2188010	Cl	0.7764550	10.9550480	14.3190600
C	-3.4926570	7.6203050	8.8083020	C	3.1261810	9.4233140	13.6305950
C	-4.7301710	7.9147030	8.0566220	O	4.0104940	9.3797350	14.3633380
C	-7.0935680	8.4691690	6.6211880				

5. References

(1) G. M. Sheldrick, *Acta Crystallogr. Sect. A Found. Crystallogr.* 2008, **64**, 112–122.

(2) G. M. Sheldrick, *Acta Crystallogr. Sect. C Struct. Chem.* 2015, **71**, 3–8.

(3) E. Pacholska-Dudziak, G. Vetter, A. Góratowska, A. Białońska, L. Latos-Grażyński, *Chem. Eur. J*. 2020, **26**, 16011–16018.

(4) E. Pacholska-Dudziak, L. Szterenberg, L. Latos-Grażyński, *Chem. Eur. J.* 2011, **17**, 3500–3511.

(5) Y.-S. Lin, G.-D. Li, S.-P. Mao, J.-D. Chai, *J. Chem. Theory Comput.* 2013, **9**, 263–272.

(6) F. Weigend and R. Ahlrichs, *Phys. Chem. Chem. Phys*. 2005, **7**, 3297–3305.

(7) F. Neese, F. Wennmohs, A. Hansen, U. Becker, *Chem. Phys.* 2009, **356**, 98–109.

(8) F. Neese, *WIREs: Comput. Mol. Sci.* 2017, **8**, e1327.

(9) W. Zou, Molden2AIM script, https://github.com/zorkzou/Molden2AIM accessed on 2023/11/14.

(10) E. D. Glendening, C. R. Landis, F. Weinhold, *J. Comput. Chem.* 2013, **34**, 1363–1374.

(11) T. A. Keith, T. K. Gristmill, AIMAII (Version 16.10.31) Software, Overland Park KS, USA, 2016 (http://aim.tkgristmill.com).

(12) T. Lu, F. Chen, *J. Comput. Chem.* 2012, **33**, 580–592.
(13) M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, G. A. Petersson, H. Nakatsuji, X. Li, M. Caricato, A. V. Marenich, J. Bloino, B. G. Janesko, R. Gomperts, B. Mennucci, H. P. Hratchian, J. V. Ortiz, A. F. Izmaylov, J. L. Sonnenberg, D. Williams-Young, F. Ding, F. Lipparini, F. Egidi, J. Goings, B. Peng, A. Petrone, T. Henderson, D. Ranasinghe, V. G. Zakrzewski, J. Gao, N. Rega, G. Zheng, W. Liang, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, K. Throssell, J. A. Montgomery, Jr., J. E. Peralta, F. Ogliaro, M. J. Bearpark, J. J. Heyd, E. N. Brothers, K. N. Kudin, V. N. Staroverov, T. A. Keith, R. Kobayashi, J. Normand, K. Raghavachari, A. P. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, J. M. Millam, M. Klene, C. Adamo, R. Cammi, J. W. Ochterski, R. L. Martin, K. Morokuma, O. Farkas, J. B. Foresman, and D. J. Fox, *Gaussian, Inc.*, Wallingford CT, 2016**.**
(14) G. Vetter, A. Białońska, P. Krzyszowska, S. Koniarz, E. Pacholska-Dudziak, *Chem. Eur. J*. 2022, **28**, e202201513.
(15) T. Sarma, B. S. Kumar, P. K. Panda, *Angew. Chem. Int. Ed*. 2015, **54**, 14835–14839.
(16) R. F. W. Bader, *Chem. Rev*. 1991, **91**, 893–928.
(17) C. Lepetit, P. Fau, K. Fajerwerg, M. L. Kahn, B. Silvi, *Coord. Chem. Rev.* 2017, **345**, 150–181.
(18) A. E. Reed, F. Weinhold, *J. Chem. Phys.* 1983, **78**, 4066–4073.
(19) A. Srinivasan, M. Toganoh, T. Niino, A. Osuka, H. Furuta, *Inorg. Chem.* 2008, **47**, 11305–11313.
(20) C. R. Groom, I. J. Bruno, M. P. Lightfoot, S. C. Ward, *Acta Crystallogr. Sect. B Struct. Sci. Cryst. Eng. Mater.* 2016, **72**, 171–179.