Electronic Supplementary Information

N^N^C-Cyclometalated rhodium(III) complexes with isomeric pyrimidine-based ligands: unveiling the impact of isomerism on structural motifs, luminescence and cytotoxicity

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NMR data

Figure S1. ^{1}H NMR spectrum of 4-(3,5-dimethyl-1*H*-pyrazol-1-yl)-2,5-diphenylpyrimidine (**HL[2,5]**).
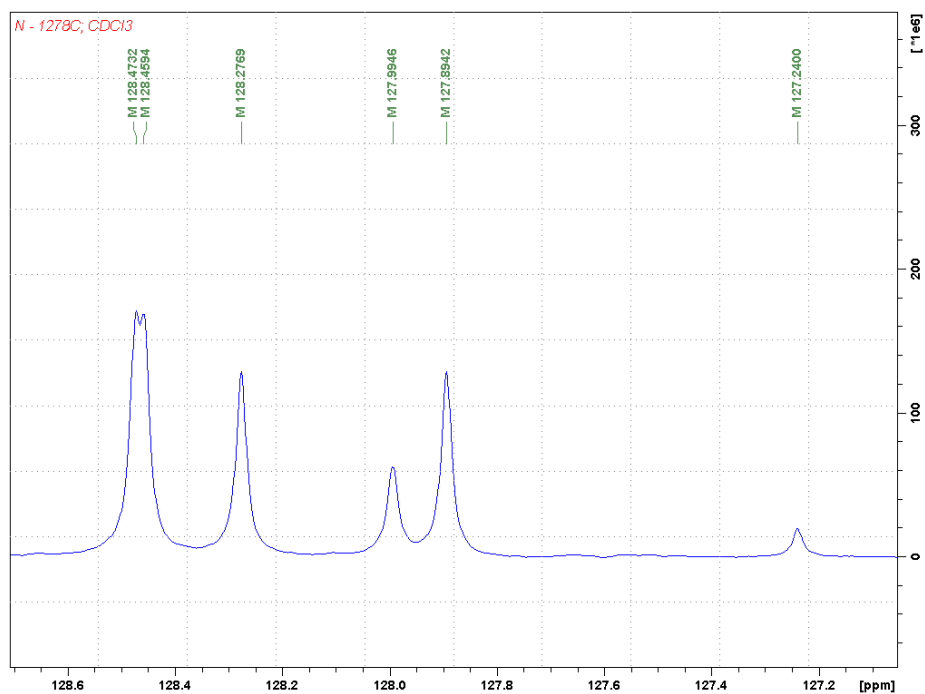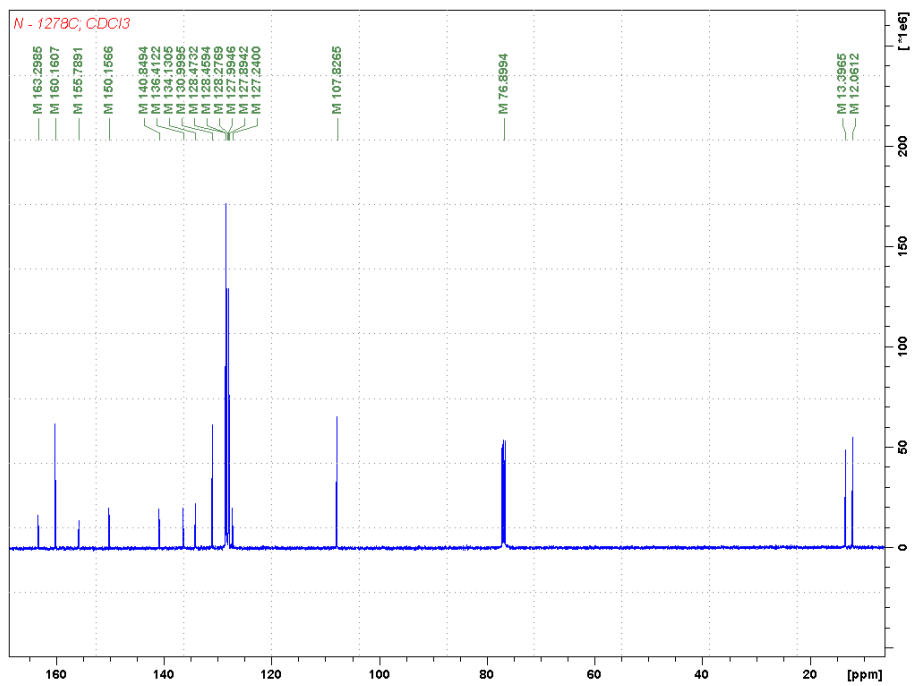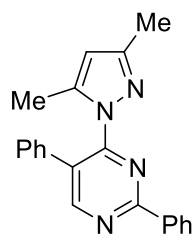
Figure S2. ^{13}C NMR spectrum of 4-(3,5-dimethyl-1*H*-pyrazol-1-yl)-2,5-diphenylpyrimidine (**HL**^{2,5}).
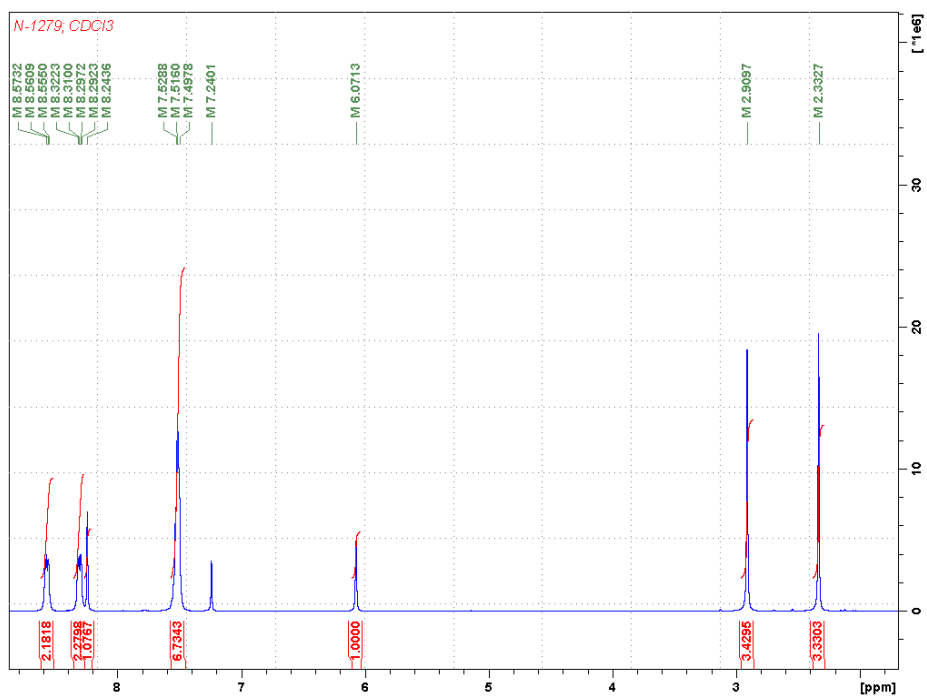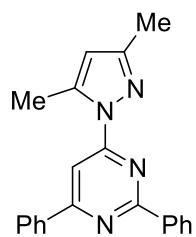
Figure S3. ^{1}H NMR spectrum of 4-(3,5-dimethyl-1*H*-pyrazol-1-yl)-2,6-diphenylpyrimidine (**HL^{2,6}**).
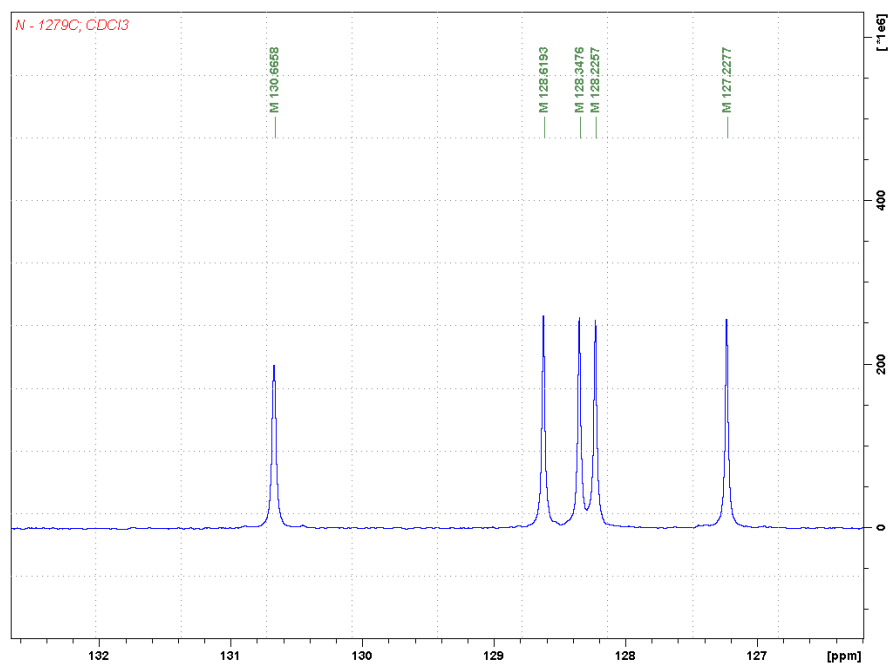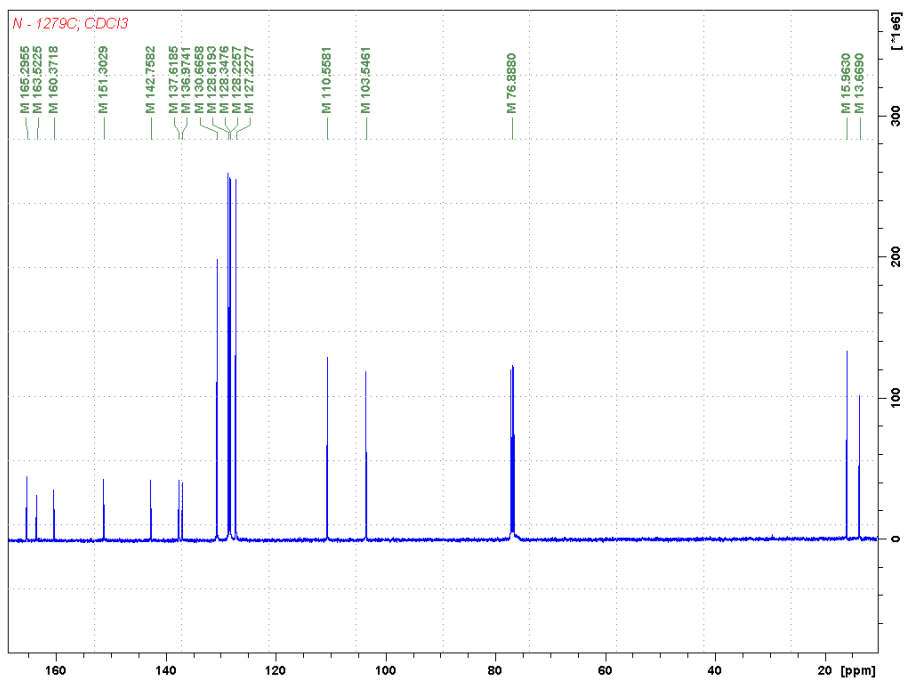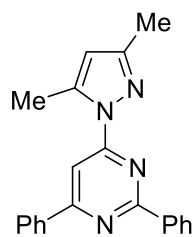
Figure S4. ^{13}C NMR spectrum of 4-(3,5-dimethyl-1*H*-pyrazol-1-yl)-2,6-diphenylpyrimidine (**HL^{2,6}**).

IR spectra
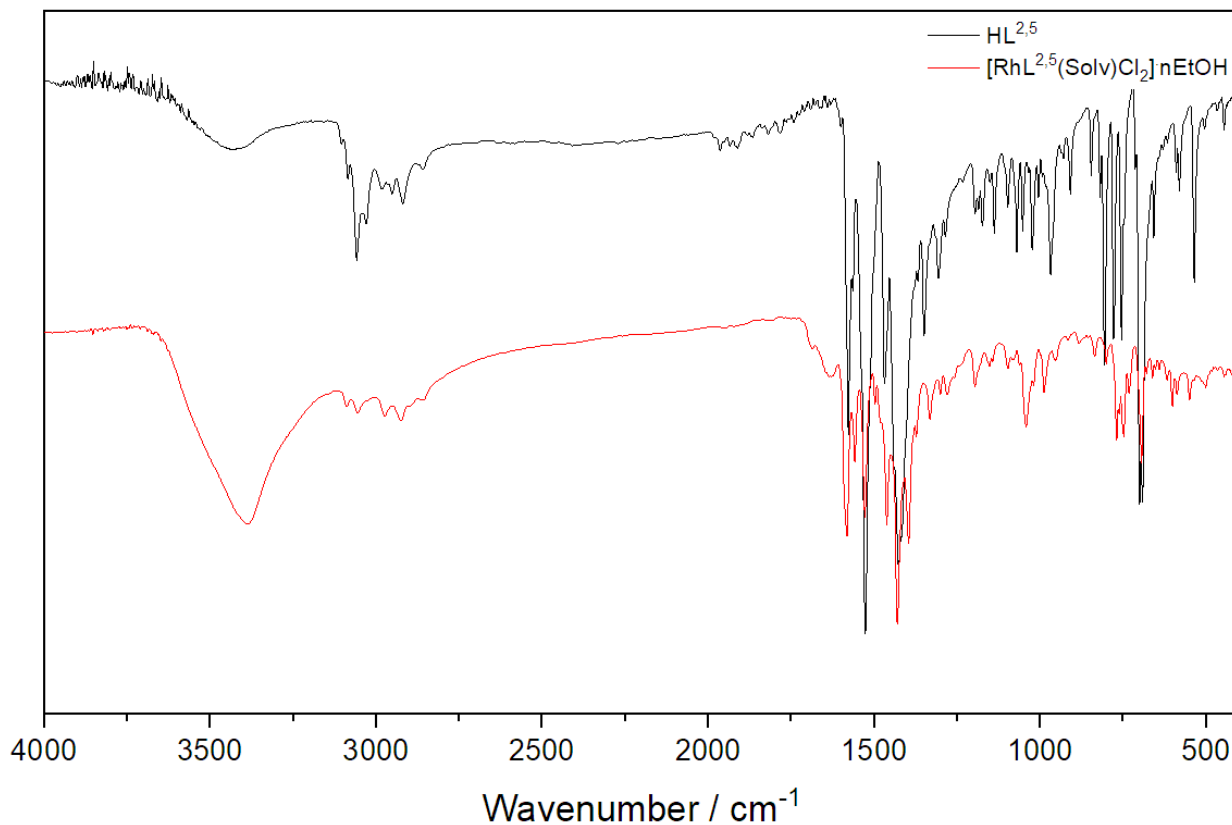
Figure S5. IR spectra of 4-(3,5-dimethyl-1H-pyrazol-1-yl)-2,5-diphenylpyrimidine (**HL^{2,5}**) and **[RhL^{2,5}(Solv)Cl$_2$]·nEtOH**.
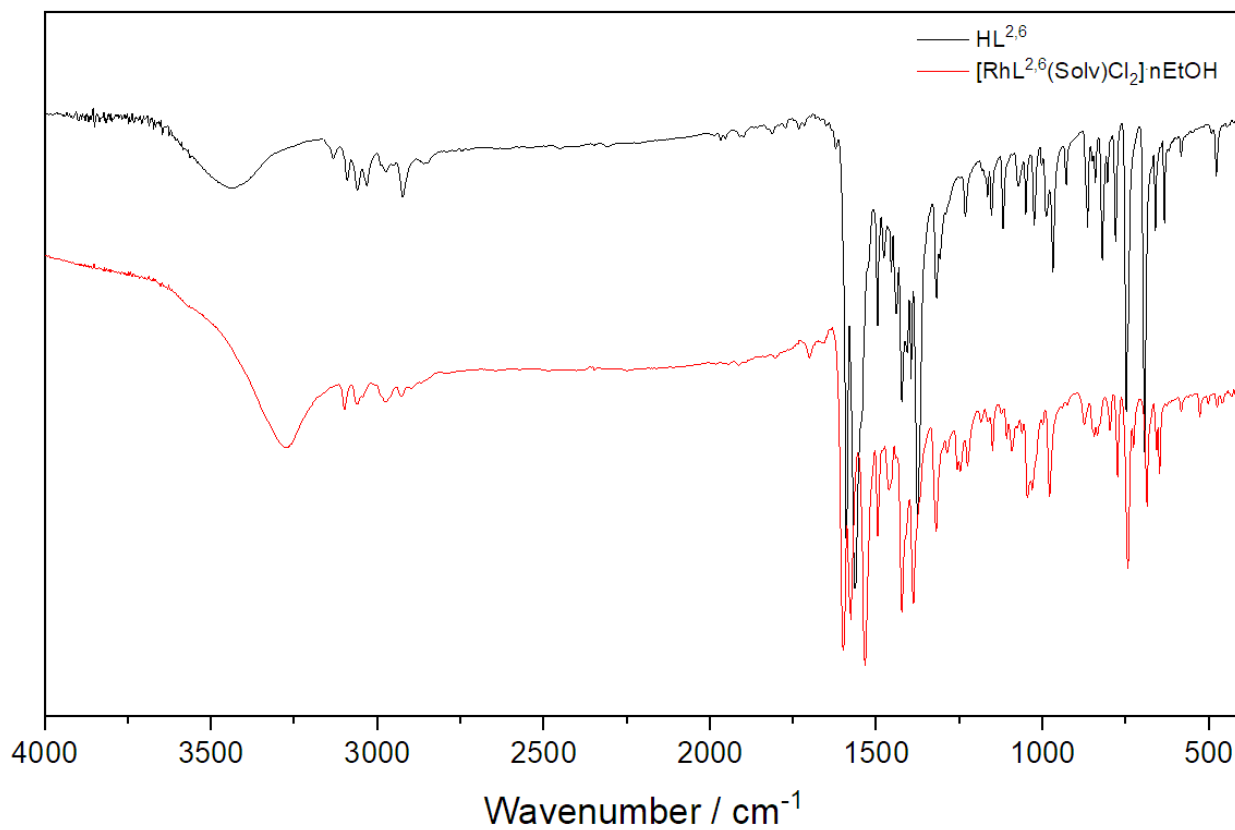
Figure S6. IR spectra of 4-(3,5-dimethyl-1H-pyrazol-1-yl)-2,6-diphenylpyrimidine (**HL^{2,6}**) and **[RhL^{2,6}(Solv)Cl$_2$]·nEtOH**.
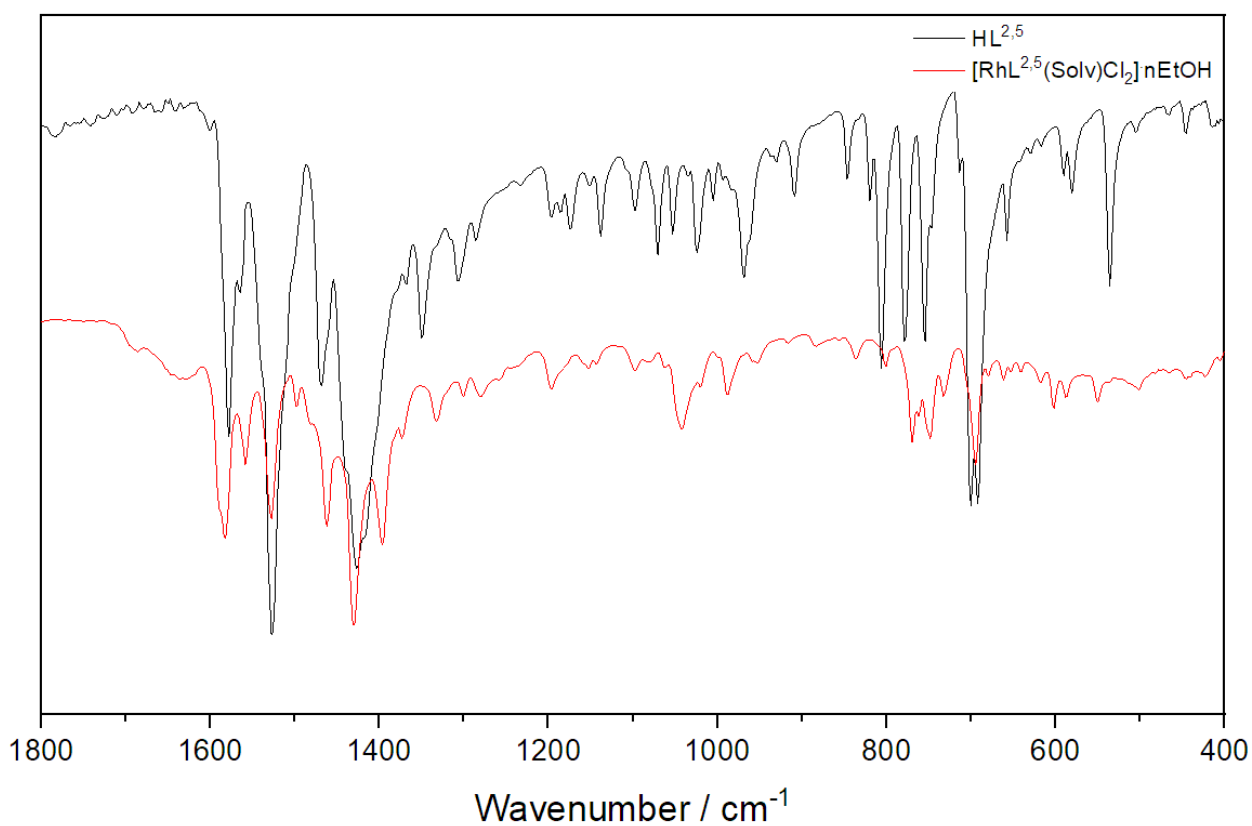
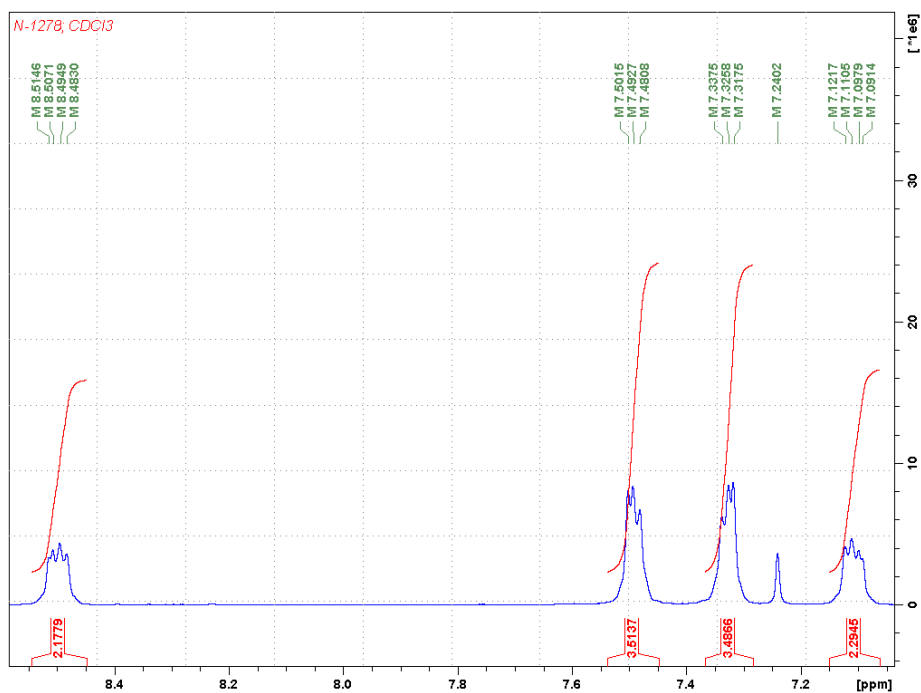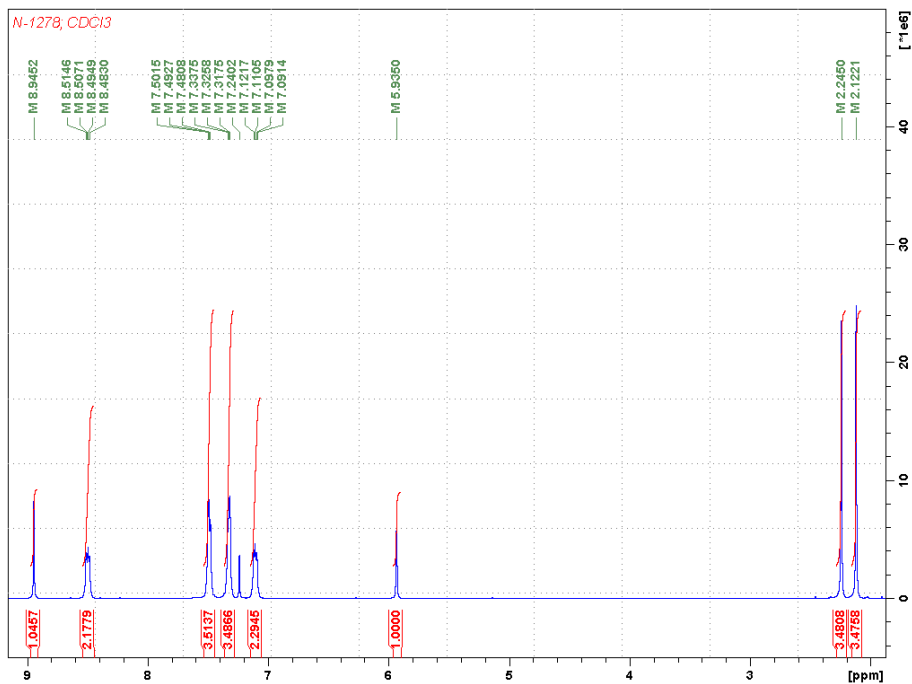Figure S7. Comparison of IR spectra of 4-(3,5-dimethyl-1*H*-pyrazol-1-yl)-2,5-diphenylpyrimidine (**HL^{2,5}**) and **[RhL^{2,5}(Solv)Cl$_2$]·nEtOH** in the 1800 – 400 cm^{-1} range.
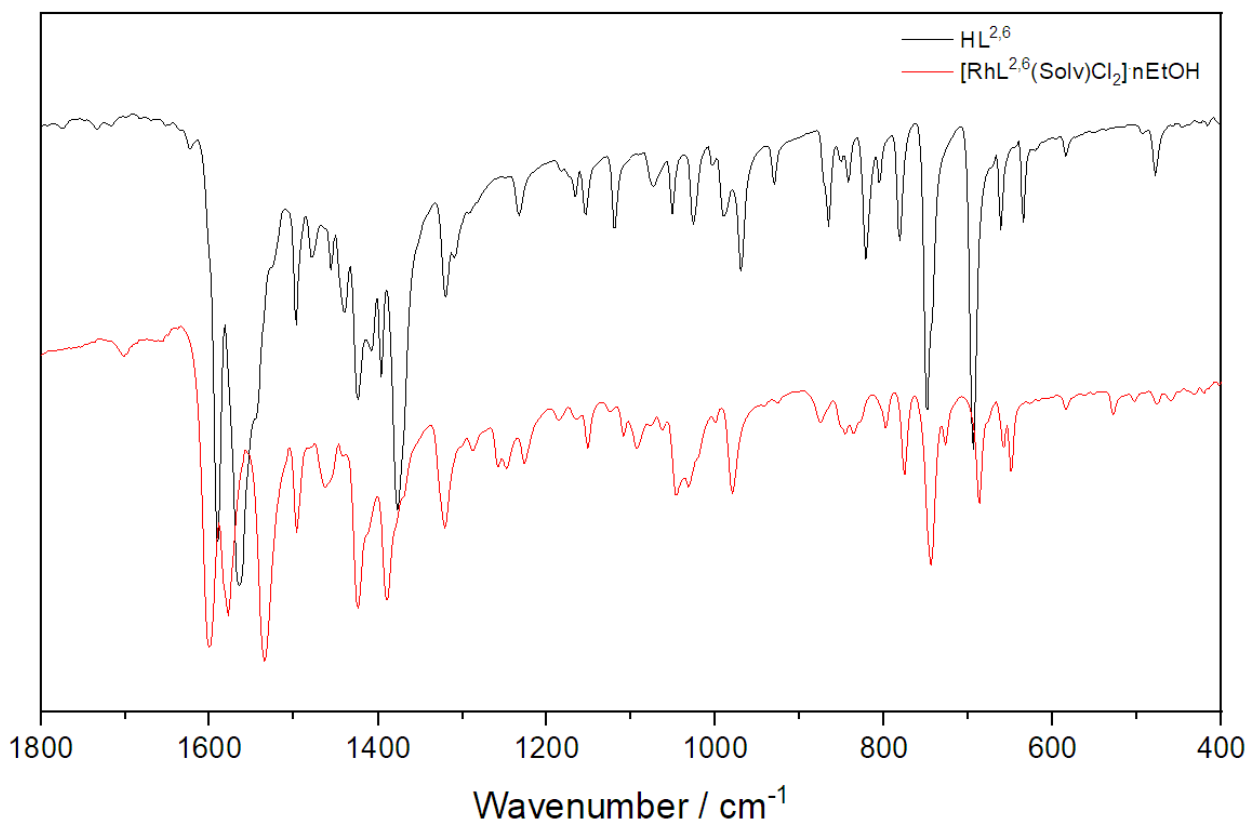
Figure S8. Comparison of IR spectra of 4-(3,5-dimethyl-1*H*-pyrazol-1-yl)-2,6-diphenylpyrimidine (**HL^{2,6}**) and **[RhL^{2,6}(Solv)Cl$_2$]·nEtOH** in the 1800 – 400 cm^{-1} range.

Structural data

Table S1. Crystal data and structure refinement for **HL^{2,5}**, **HL^{2,6}**, **[RhL^{2,5}(Solv)Cl$_2$]·nEtOH**, and **[RhL^{2,6}(Solv)Cl$_2$]·nEtOH**.

|	HL^{2,5}	HL^{2,6}	[RhL^{2,5}(Solv)Cl$_2$]·nEtOH,	[RhL^{2,6}(Solv)Cl$_2$]·nEtOH,
Empirical formula	C$_{21}$H$_{18}$N$_4$	C$_{21}$H$_{18}$N$_4$	C$_{23}$H$_{24.4}$Cl$_2$N$_4$O$_{1.7}$Rh	C$_{23}$H$_{23.8}$Cl$_2$N$_4$O$_{1.4}$Rh
Formula weight	326.39	326.39	557.87	552.47
Crystal system	monoclinic	orthorhombic	triclinic	triclinic
Space group, Z	P2$_1$/n, *8*	P2$_1$2$_1$2$_1$, *4*	P-1, *2*	P-1, *2*
a(Å)	17.1096(3)	5.0408(4)	8.8156(3)	8.7080(3)
b(Å)	7.69100(10)	16.6643(13)	10.9113(4)	9.5487(4)
c(Å)	26.8277(6)	19.8837(18)	12.2108(5)	14.4311(6)
α/°	90	90	103.5000(10)	84.660(2)
β/°	104.2630(10)	90	92.4590(10)	80.9050(10)
γ/°	90	90	91.6840(10)	79.224(2)
V(Å3)	3421.44(11)	1670.3(2)	1140.11(7)	1161.47(8)
dCalc(g/cm3)	1.267	1.298	1.618	1.575
μ/mm^{-1}	0.077	0.079	1.010	0.990
F(000)	1376.0	688.0	561.0	557.0
Crystal size (mm)	0.180 × 0.180 × 0.100	0.270 × 0.050 × 0.010	0.140 × 0.070 × 0.030	0.120 × 0.060 × 0.040
2Θ range for data collection/°	3.472 - 66.302	3.188 -52.742	4.512 -61.116	4.812 to 61.368
Index ranges	-26 ≤ h ≤ 25 -11 ≤ k ≤ 11 -23 ≤ l ≤ 41	-5 ≤ h ≤ 6 -18 ≤ k ≤ 20 -24 ≤ l ≤ 24	-10 ≤ h ≤ 12 -15 ≤ k ≤ 14 -17 ≤ l ≤ 17	-12 ≤ h ≤ 12 -13 ≤ k ≤ 13 -20 ≤ l ≤ 20
Reflections collected	48966	7858	14266	23075
Independent reflections (*R*int)	13029 [R$_{int}$ = 0.0622]	3400 [R$_{int}$ = 0.0460]	6959 [R$_{int}$ = 0.0295]	7138 [R$_{int}$ = 0.0433]
Completeness to theta = 50.5°	100 %	100 %	99.8 %	99.9 %
Data / restraints / parameters	13029/0/455	3400/0/228	6959/1/317	7138/6/297
Goodness-of-fit on *F*2	1.023	1.044	1.068	1.047
Final *R* indices (I>=2σ (I))	R$_1$ = 0.0627, wR$_2$ = 0.1362	R$_1$ = 0.0543, wR$_2$ = 0.1025	R$_1$ = 0.0363, wR$_2$ = 0.0785	R$_1$ = 0.0390, wR$_2$ = 0.0857
R indices (all data)	R$_1$ = 0.1161, wR$_2$ = 0.1658	R$_1$ = 0.0881, wR$_2$ = 0.1159	R$_1$ = 0.0483, wR$_2$ = 0.0834	R$_1$ = 0.0532, wR$_2$ = 0.0917
Largest diff. peak and hole (e/Å3)	0.32/-0.24	0.18/-0.21	0.78/-0.57	0.69/-0.53
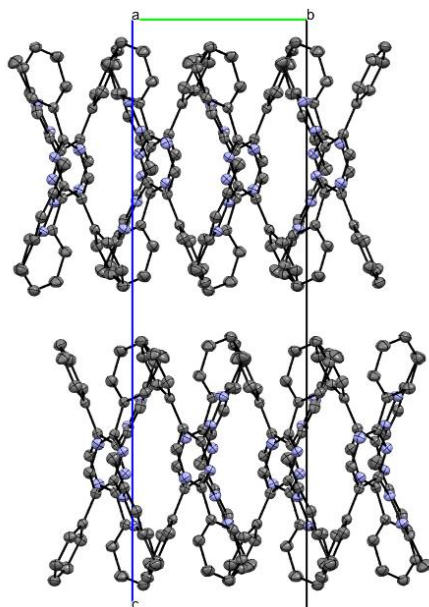
Figure S9. **Packing of HL²,⁵** (view along the *a* axis, two supramolecular layers are shown). Hydrogen atoms are omitted for clarity.
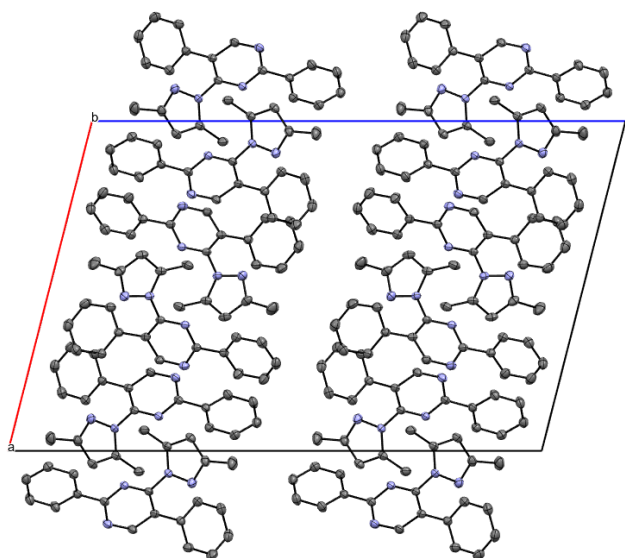
Figure S10. **Packing of HL²,⁵** (view along the *b* axis, two supramolecular layers are shown). Hydrogen atoms are omitted for clarity.
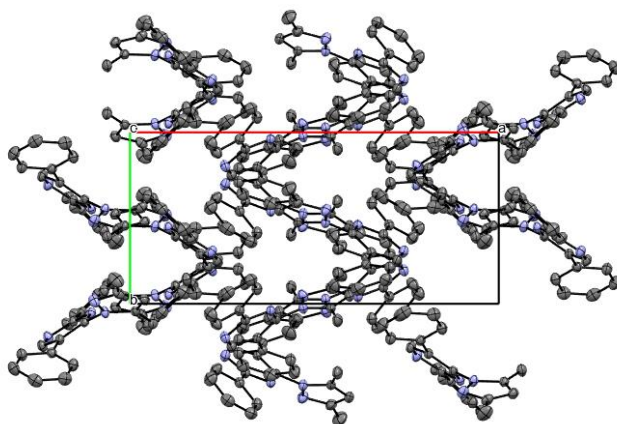
Figure S11. **Packing of HL²,⁵** (view along the *c* axis). Hydrogen atoms are omitted for clarity.
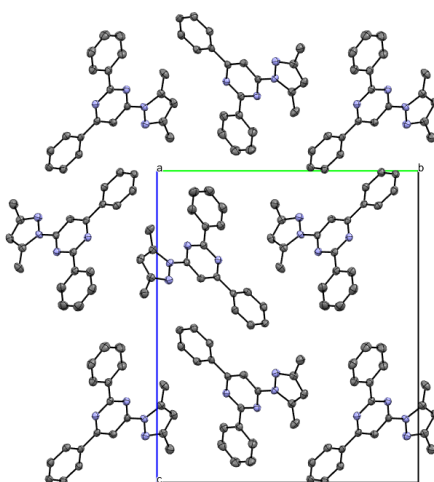
Figure S12. Packing of **HL^{2,6}** (view along the *a* axis). Hydrogen atoms are omitted for clarity.
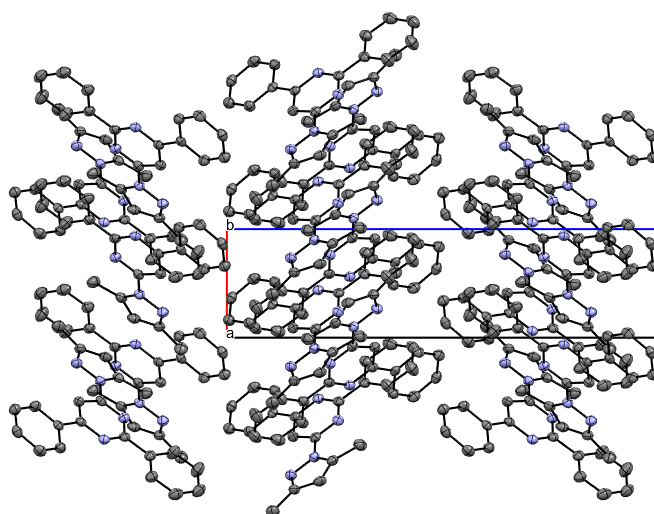
Figure S13. Packing of **HL^{2,6}** (view along the *b* axis). Hydrogen atoms are omitted for clarity.
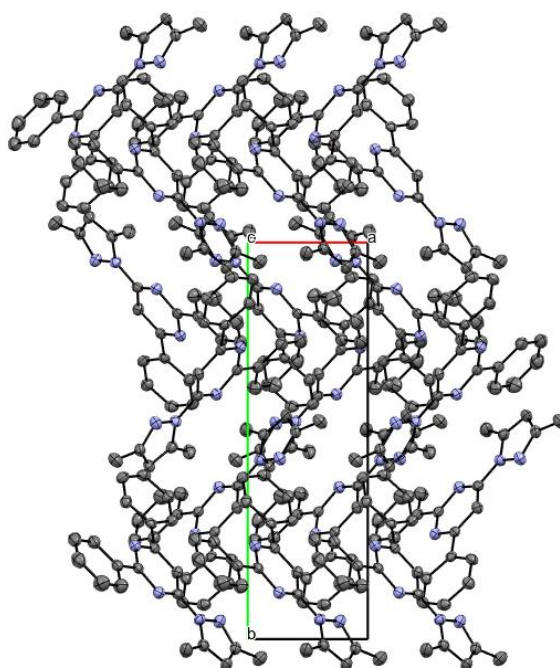
Figure S14. Packing of **HL^{2,6}** (view along the *c* axis). Hydrogen atoms are omitted for clarity.
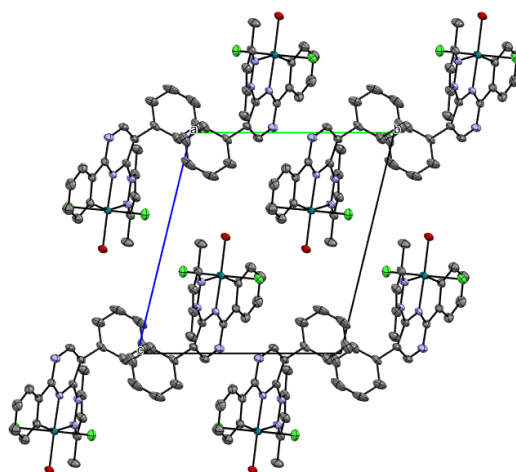
Figure S15. Packing of **[RhL^{2,5}(Solv)Cl$_2$]·nEtOH** (view along the *a* axis). Hydrogen atoms and EtOH molecules are omitted for clarity.
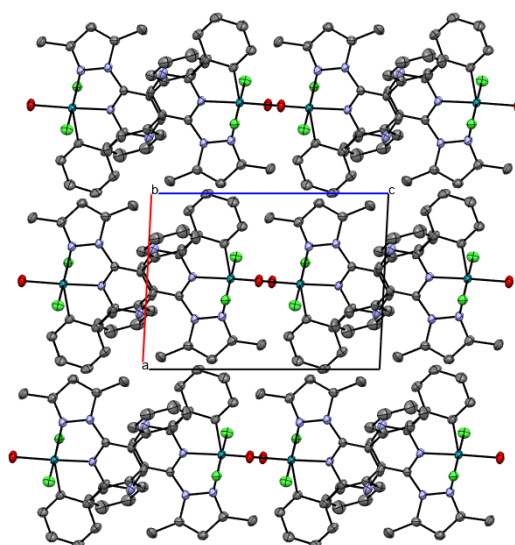
Figure S16. Packing of **[RhL^{2,5}(Solv)Cl$_2$]·nEtOH** (view along the *b* axis). Hydrogen atoms and EtOH molecules are omitted for clarity.
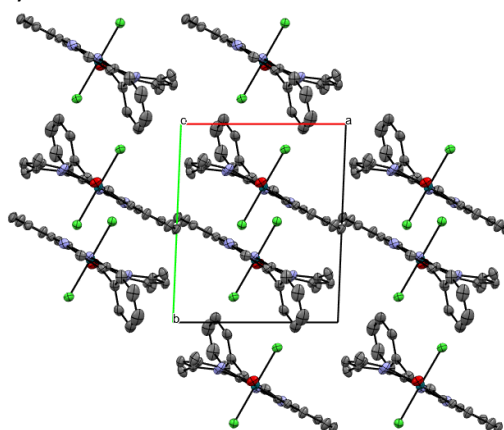
Figure S17. Packing of **[RhL^{2,5}(Solv)Cl$_2$]·nEtOH** (view along the *c* axis). Hydrogen atoms and EtOH molecules are omitted for clarity.
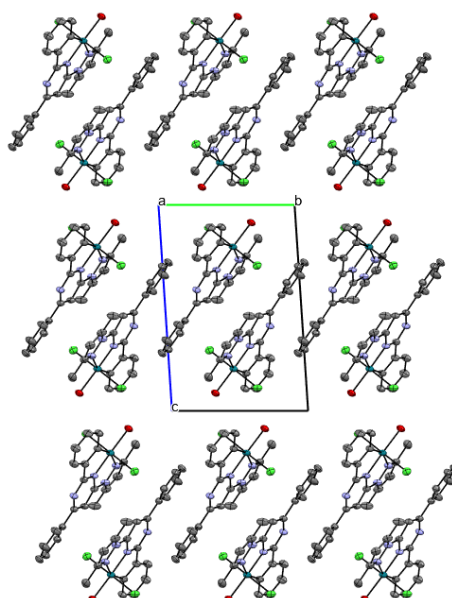
Figure S18. Packing of **[RhL^{2,6}(Solv)Cl$_2$]·nEtOH** (view along the *a* axis). Hydrogen atoms and EtOH molecules are omitted for clarity.
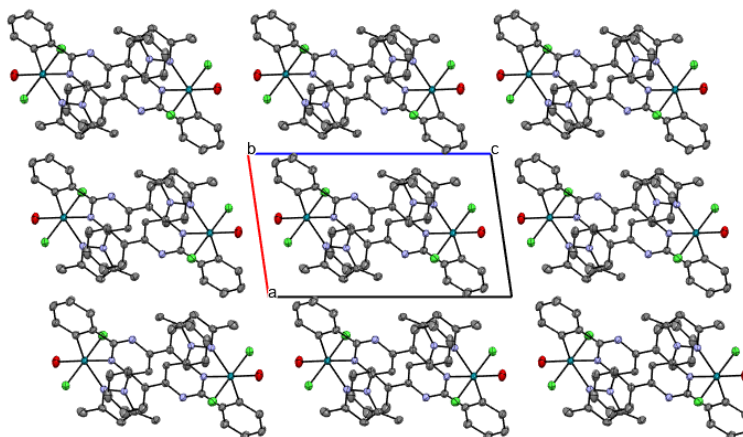
Figure S19. Packing of **[RhL^{2,6}(Solv)Cl$_2$]·nEtOH** (view along the *b* axis). Hydrogen atoms and EtOH molecules are omitted for clarity.
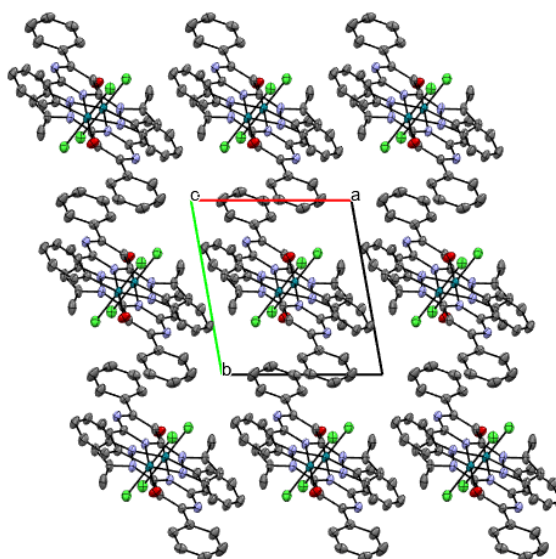
Figure S20. Packing of **[RhL^{2,6}(Solv)Cl$_2$]·nEtOH** (view along the *c* axis). Hydrogen atoms and EtOH molecules are omitted for clarity.
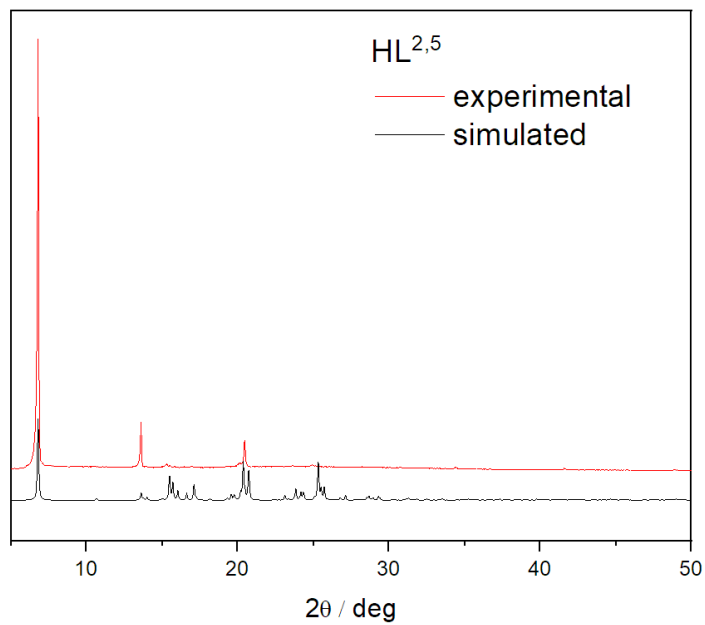
Figure S21. X-ray powder diffraction patterns of **HL^{2,5}**.
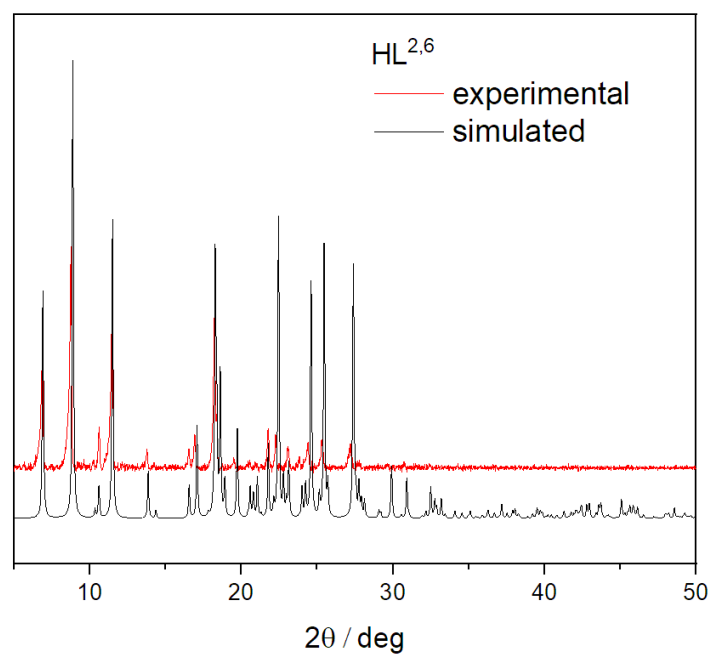
Figure S22. X-ray powder diffraction patterns of **HL^{2,6}**.
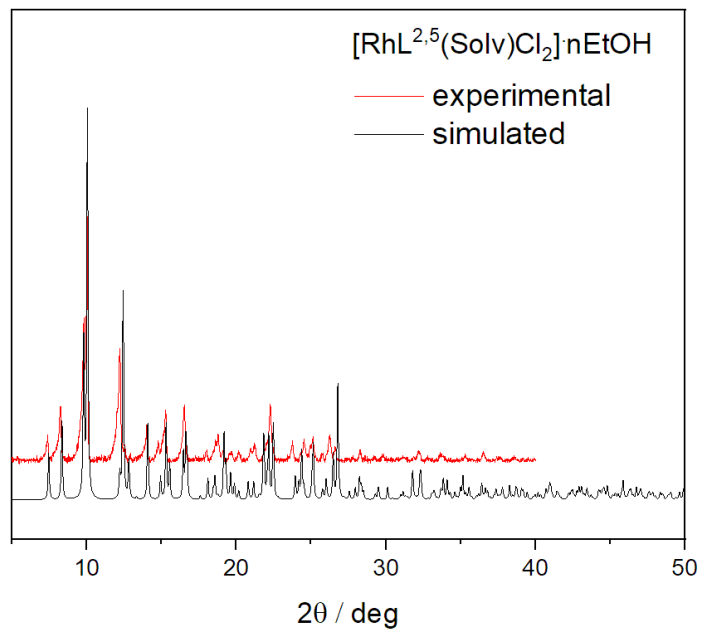
Figure S23. X-ray powder diffraction patterns of **[RhL^{2,5}(Solv)Cl$_2$]·nEtOH**.
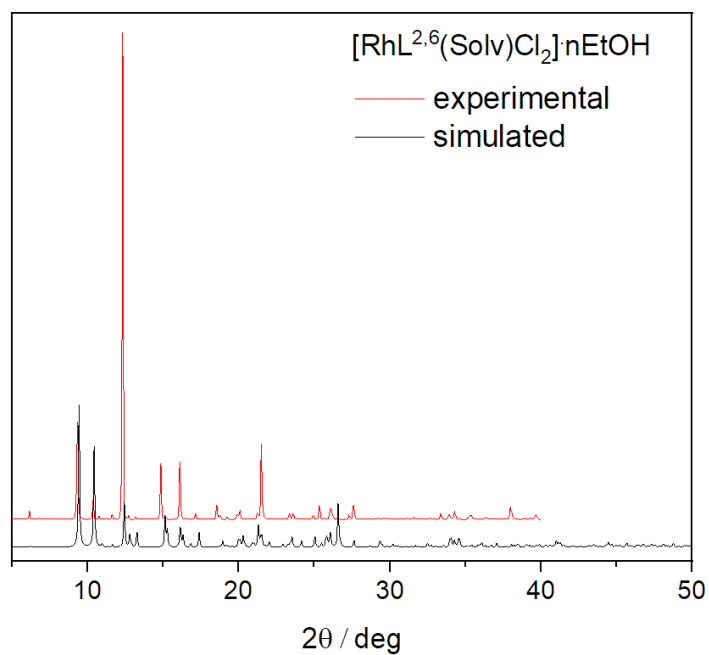
Figure S24. X-ray powder diffraction patterns of **[RhL^{2,6}(Solv)Cl$_2$]·nEtOH**.

Computational and photophysical data
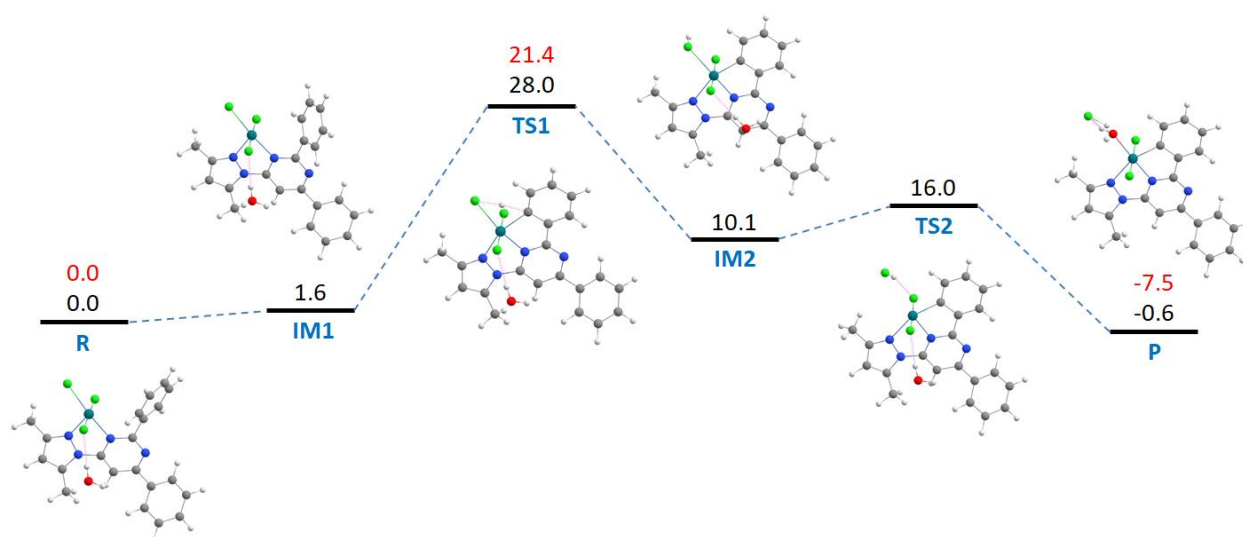
Figure S25. The computed C–H bond activation path for the rhodium(III) complex with **HL^{2,6}**. Relative energies calculated in PCM (EtOH) and in the gas phase are shown in black and red, respectively.
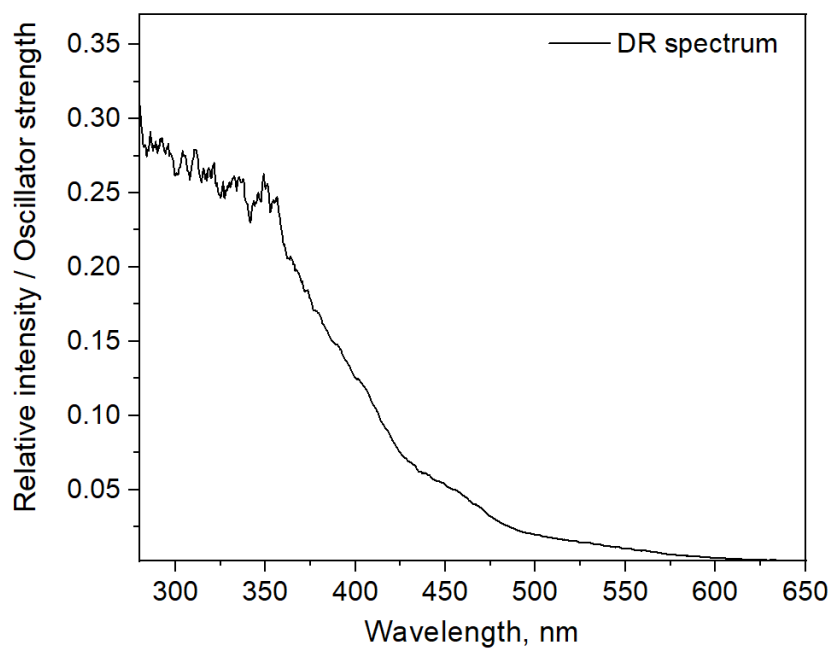
Figure S26. Experimental diffuse reflectance (DR) spectrum of the **[RhL^{2,6}(Solv)Cl$_2$]·nEtOH** complex.

Model	ExpDec2	
Equation	y = A1*exp(-x/t1) + A2*exp(-x/t2) + y0	
Reduced Chi-Sqr	9.23749	
Adj. R-Square	0.92047	
	Value	Standard Error
C	y0	3.89621	0.189
	A1	14.92257	2.45282
	t1	48.04865	6.58007
	A2	7869.86541	806.54917
	t2	6.33553	0.14199

$\tau_1 = 48$ ns (36%), $\tau_2 = 6$ ns (64%)
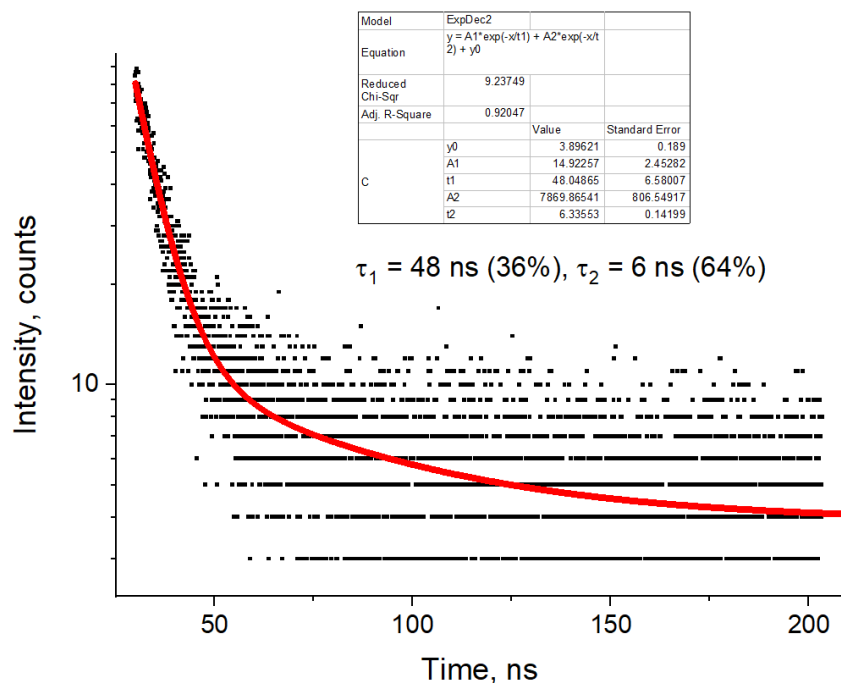
Figure S27. Luminescence decay kinetics of the **[RhL^{2,5}(Solv)Cl$_2$]·nEtOH** complex, λ_{ex} = 390 nm, λ_{reg} = 450 nm

Model	ExpDec1	
Equation	y = A1*exp(-x/t1) + y0	
Reduced Chi-Sqr	6.26944	
Adj. R-Square	0.94301	
	Value	Standard Error
S1	y0	1	0
	A1	169.85939	8.55276
	t1	0.04584	0.00141

$\tau = 46$ μs
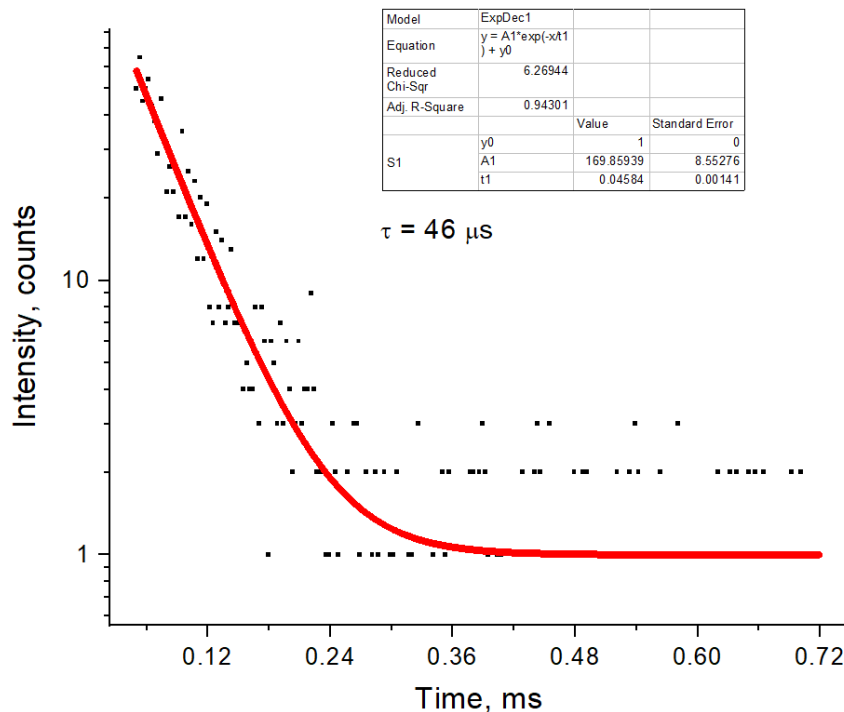
Figure S28. Luminescence decay kinetics of the **[RhL^{2,5}(Solv)Cl$_2$]·nEtOH** complex, λ_{ex} = 440 nm, λ_{reg} = 520 nm

Table S2. Optimized geometries of the ground state of rhodium(III) complexes with **HL[2,5]** from Figure 4 in Cartesian (XYZ) coordinates as calculated in Gaussian at the ωB97XD/Stuttgart RSC 1997/6-31+g(d) level of theory **in EtOH continuum solvation model**.

R			
Rh	1.476454000000	0.907738000000	0.002376000000
Cl	1.880220000000	0.958925000000	-2.315005000000
O	-0.953631000000	-1.735861000000	2.624223000000
N	0.190515000000	-0.663306000000	-0.308054000000
N	-0.208825000000	1.856846000000	-0.267996000000
C	-2.108022000000	-1.281330000000	-0.323204000000
N	-1.281739000000	1.060157000000	-0.598589000000
H	4.536030000000	-2.383453000000	2.013331000000
C	2.616947000000	-2.876713000000	-1.319281000000
C	1.970368000000	-2.323654000000	-0.210134000000
C	-1.638423000000	-2.595250000000	-0.415483000000
C	-0.519609000000	3.114724000000	-0.556374000000
N	-0.355095000000	-2.937076000000	-0.465592000000
C	-1.106572000000	-0.316531000000	-0.418068000000
C	3.959234000000	-3.232473000000	-1.229536000000
C	2.660684000000	-2.152694000000	0.993202000000
C	-1.811702000000	3.130640000000	-1.112693000000
C	-2.263086000000	1.835015000000	-1.176080000000
C	4.653528000000	-3.052004000000	-0.032198000000
C	0.533864000000	-1.960543000000	-0.321796000000
C	4.003428000000	-2.517501000000	1.077659000000
Cl	1.037693000000	0.814693000000	2.336300000000
H	-0.364350000000	-0.965206000000	2.640169000000
H	-0.439998000000	-2.455049000000	3.003827000000
H	4.462976000000	-3.650828000000	-2.094676000000
H	5.700559000000	-3.329577000000	0.034938000000
H	-2.333840000000	4.001846000000	-1.477307000000
H	2.074126000000	-3.015316000000	-2.248940000000
C	-3.501648000000	1.347188000000	-1.843405000000
H	-4.319297000000	1.200088000000	-1.135180000000
H	-3.804840000000	2.106217000000	-2.565785000000
H	-3.328505000000	0.410898000000	-2.376245000000
C	0.401684000000	4.261327000000	-0.347126000000
H	1.215313000000	4.227420000000	-1.076371000000
H	-0.147521000000	5.195207000000	-0.468379000000
H	0.848141000000	4.222568000000	0.647952000000
H	-2.356298000000	-3.410802000000	-0.417399000000
C	-3.529553000000	-1.026440000000	-0.004452000000
C	-3.847721000000	-0.199077000000	1.078475000000
C	-4.551365000000	-1.652317000000	-0.724119000000
C	-5.179544000000	0.024668000000	1.415192000000
C	-5.882070000000	-1.427185000000	-0.383077000000
C	-6.198519000000	-0.584545000000	0.682439000000
H	-3.054421000000	0.265221000000	1.656913000000
H	-4.308344000000	-2.289098000000	-1.569741000000
H	-5.421251000000	0.671826000000	2.251892000000
H	-6.671922000000	-1.904710000000	-0.953516000000

H	-7.236782000000	-0.405608000000	0.942245000000
H	2.155963000000	-1.731883000000	1.856640000000
Cl	3.150489000000	2.500054000000	0.393743000000

IM1

Rh	-1.375248000000	-0.653503000000	0.353622000000
Cl	-1.988720000000	-0.964071000000	-1.894670000000
O	2.112958000000	-1.915800000000	2.607104000000
N	-0.107700000000	0.813939000000	-0.198762000000
N	0.269346000000	-1.690561000000	0.047218000000
C	2.175881000000	1.443256000000	-0.277011000000
N	1.347481000000	-0.927853000000	-0.359204000000
H	-4.878593000000	1.150947000000	0.881110000000
C	-2.438031000000	3.303514000000	-1.233895000000
C	-1.936464000000	2.360982000000	-0.335996000000
C	1.681578000000	2.747808000000	-0.422100000000
C	0.551419000000	-2.963359000000	-0.195827000000
N	0.394256000000	3.076858000000	-0.494696000000
C	1.185070000000	0.459819000000	-0.288200000000
C	-3.815058000000	3.457176000000	-1.381023000000
C	-2.828686000000	1.597397000000	0.434796000000
C	1.821289000000	-3.029256000000	-0.797884000000
C	2.293911000000	-1.747622000000	-0.932418000000
C	-4.698075000000	2.674631000000	-0.637526000000
C	-0.482620000000	2.095692000000	-0.317845000000
C	-4.203629000000	1.747613000000	0.277602000000
Cl	-0.703664000000	-0.272629000000	2.611260000000
H	1.235841000000	-1.504194000000	2.655504000000
H	2.407122000000	-1.987913000000	3.520022000000
H	-4.199234000000	4.182960000000	-2.090440000000
H	-5.768503000000	2.793928000000	-0.765610000000
H	2.316030000000	-3.925273000000	-1.139838000000
H	-1.751400000000	3.891415000000	-1.833336000000
Cl	-3.003064000000	-2.190953000000	1.083570000000
C	3.516868000000	-1.310355000000	-1.660746000000
H	4.355651000000	-1.135574000000	-0.984237000000
H	3.791194000000	-2.108412000000	-2.351779000000
H	3.338510000000	-0.399713000000	-2.235127000000
C	-0.376062000000	-4.081733000000	0.114332000000
H	-1.308678000000	-3.971011000000	-0.443667000000
H	0.096162000000	-5.028586000000	-0.147759000000
H	-0.625707000000	-4.084087000000	1.177912000000
H	-2.475509000000	0.996726000000	1.282260000000
H	2.389896000000	3.570894000000	-0.457375000000
C	3.614430000000	1.223933000000	-0.007331000000
C	3.998380000000	0.423615000000	1.075196000000
C	4.588287000000	1.853539000000	-0.788588000000
C	5.349858000000	0.245001000000	1.357842000000
C	5.937966000000	1.668427000000	-0.502171000000
C	6.321102000000	0.862892000000	0.570050000000
H	3.250603000000	-0.084478000000	1.680134000000
H	4.294085000000	2.463315000000	-1.637941000000
H	5.643318000000	-0.382521000000	2.193234000000
H	6.689421000000	2.147937000000	-1.120824000000

H	7.373786000000	0.715168000000	0.788527000000

TS1

Rh	-1.533602000000	-0.499505000000	0.168429000000
Cl	-1.781120000000	-1.026622000000	-2.119009000000
O	1.764759000000	-1.311148000000	2.854456000000
N	-0.144068000000	0.821630000000	-0.250781000000
N	0.233531000000	-1.656111000000	0.173645000000
C	2.128056000000	1.446509000000	-0.266695000000
N	1.303046000000	-0.935434000000	-0.309810000000
H	-4.899522000000	0.529279000000	-0.141656000000
C	-2.522428000000	3.567973000000	-0.471062000000
C	-1.986758000000	2.298857000000	-0.251742000000
C	1.630554000000	2.756527000000	-0.354798000000
C	0.522172000000	-2.935826000000	0.021883000000
N	0.343697000000	3.095716000000	-0.393819000000
C	1.146251000000	0.454071000000	-0.294210000000
C	-3.899533000000	3.744041000000	-0.550636000000
C	-2.831310000000	1.168356000000	-0.091898000000
C	1.785404000000	-3.059900000000	-0.593648000000
C	2.251753000000	-1.788841000000	-0.829604000000
C	-4.735354000000	2.638955000000	-0.437778000000
C	-0.532415000000	2.104300000000	-0.290474000000
C	-4.207556000000	1.362879000000	-0.217610000000
Cl	-1.206491000000	0.039441000000	2.465023000000
H	0.856252000000	-0.998045000000	2.719657000000
H	1.952197000000	-1.138146000000	3.782003000000
H	-4.314393000000	4.731751000000	-0.718715000000
H	-5.810563000000	2.757163000000	-0.524467000000
H	2.280077000000	-3.977223000000	-0.874847000000
H	-1.845089000000	4.406502000000	-0.595428000000
Cl	-3.509764000000	-1.818451000000	0.778976000000
C	3.462898000000	-1.391091000000	-1.601538000000
H	4.310417000000	-1.167664000000	-0.950522000000
H	3.736027000000	-2.226274000000	-2.248059000000
H	3.268642000000	-0.518416000000	-2.227947000000
C	-0.445903000000	-3.994776000000	0.420197000000
H	-1.199874000000	-4.123383000000	-0.362831000000
H	0.068308000000	-4.945479000000	0.565982000000
H	-0.960770000000	-3.716432000000	1.341950000000
H	-3.180066000000	-0.267113000000	0.474097000000
H	2.341937000000	3.577908000000	-0.360140000000
C	3.572704000000	1.223611000000	-0.028719000000
C	3.978142000000	0.467566000000	1.077367000000
C	4.528466000000	1.801447000000	-0.869404000000
C	5.335733000000	0.278966000000	1.323352000000
C	5.884333000000	1.605980000000	-0.619143000000
C	6.289646000000	0.842369000000	0.475364000000
H	3.235785000000	0.012985000000	1.730673000000
H	4.213597000000	2.378102000000	-1.734525000000
H	5.648338000000	-0.312059000000	2.178309000000
H	6.622657000000	2.043177000000	-1.283417000000
H	7.346564000000	0.686545000000	0.666435000000

IM2

Rh	-1.560373000000	-0.519443000000	0.001595000000
Cl	-1.675731000000	-0.787920000000	-2.343832000000
O	1.624166000000	-1.307140000000	2.816761000000
N	-0.148405000000	0.829289000000	-0.190246000000
N	0.350884000000	-1.732073000000	-0.000511000000
C	2.124595000000	1.464565000000	-0.130173000000
N	1.340484000000	-0.894373000000	-0.463619000000
H	-4.734229000000	0.280978000000	-0.053757000000
C	-2.605155000000	3.539090000000	-0.115046000000
C	-1.984826000000	2.287236000000	-0.100337000000
C	1.629930000000	2.776379000000	-0.089380000000
C	0.696983000000	-2.953324000000	-0.368068000000
N	0.343451000000	3.117623000000	-0.124936000000
C	1.143726000000	0.477399000000	-0.270104000000
C	-3.993379000000	3.608481000000	-0.109296000000
C	-2.734497000000	1.090229000000	-0.072222000000
C	1.899340000000	-2.916242000000	-1.108385000000
C	2.278038000000	-1.598067000000	-1.187892000000
C	-4.744607000000	2.430314000000	-0.089609000000
C	-0.533588000000	2.120199000000	-0.132926000000
C	-4.124010000000	1.178274000000	-0.069927000000
Cl	-1.493356000000	-0.337412000000	2.376688000000
H	0.707362000000	-1.150362000000	2.540944000000
H	1.686172000000	-0.912017000000	3.691808000000
H	-4.490930000000	4.572406000000	-0.122903000000
H	-5.829470000000	2.486307000000	-0.088987000000
H	2.406993000000	-3.751501000000	-1.567246000000
H	-1.999253000000	4.439866000000	-0.134021000000
Cl	-3.346879000000	-2.242832000000	0.289966000000
C	3.393713000000	-1.010624000000	-1.983933000000
H	4.294370000000	-0.864794000000	-1.383555000000
H	3.630498000000	-1.703028000000	-2.793300000000
H	3.114111000000	-0.050355000000	-2.422385000000
C	-0.163317000000	-4.126251000000	-0.040494000000
H	-0.907889000000	-4.280139000000	-0.828144000000
H	0.439884000000	-5.032440000000	0.039185000000
H	-0.690462000000	-3.963693000000	0.901663000000
H	-3.376762000000	-2.190851000000	1.582352000000
H	2.339793000000	3.594284000000	0.002461000000
C	3.568227000000	1.212063000000	0.084918000000
C	3.974637000000	0.278762000000	1.046139000000
C	4.527843000000	1.929691000000	-0.635921000000
C	5.331733000000	0.054819000000	1.262371000000
C	5.883500000000	1.702396000000	-0.413540000000
C	6.288364000000	0.761109000000	0.532362000000
H	3.230198000000	-0.272543000000	1.617389000000
H	4.216327000000	2.644745000000	-1.391910000000
H	5.642740000000	-0.673262000000	2.004743000000
H	6.621965000000	2.254812000000	-0.985545000000
H	7.345070000000	0.580185000000	0.701319000000
TS2			
Rh	-1.475413000000	-0.784097000000	0.090210000000
Cl	-1.587984000000	-1.023659000000	-2.272485000000

O	-3.072536000000	2.071212000000	3.315034000000
N	-0.118428000000	0.589281000000	-0.088035000000
N	0.434935000000	-1.957484000000	0.067357000000
C	2.135090000000	1.284091000000	-0.029442000000
N	1.421817000000	-1.096524000000	-0.359872000000
H	-4.661476000000	-0.108045000000	0.105088000000
C	-2.655476000000	3.231925000000	-0.025276000000
C	-1.992748000000	2.001831000000	-0.014740000000
C	1.607398000000	2.582796000000	-0.003234000000
C	0.793374000000	-3.164905000000	-0.326545000000
N	0.312617000000	2.889482000000	-0.048544000000
C	1.184696000000	0.267163000000	-0.168038000000
C	-4.046067000000	3.248644000000	0.009099000000
C	-2.700113000000	0.782345000000	0.027998000000
C	2.008237000000	-3.098443000000	-1.048343000000
C	2.376070000000	-1.777503000000	-1.092510000000
C	-4.755889000000	2.043546000000	0.050658000000
C	-0.539110000000	1.873023000000	-0.046462000000
C	-4.091195000000	0.814542000000	0.062237000000
Cl	-1.461719000000	-0.679287000000	2.448116000000
H	-2.618729000000	1.271876000000	3.004761000000
H	-3.425555000000	2.478249000000	2.516085000000
H	-4.578341000000	4.193707000000	0.003461000000
H	-5.841262000000	2.062583000000	0.081315000000
H	2.527892000000	-3.916836000000	-1.523687000000
H	-2.084513000000	4.154633000000	-0.053932000000
Cl	-3.799224000000	-2.863188000000	-0.497699000000
C	3.496594000000	-1.164589000000	-1.861449000000
H	4.379439000000	-0.998096000000	-1.240509000000
H	3.768206000000	-1.852459000000	-2.663564000000
H	3.204884000000	-0.212056000000	-2.308836000000
C	-0.057103000000	-4.351452000000	-0.029415000000
H	-0.316144000000	-4.871378000000	-0.955534000000
H	0.482080000000	-5.054918000000	0.610841000000
H	-0.976641000000	-4.045080000000	0.473087000000
H	-3.178523000000	-2.372184000000	-1.539954000000
H	2.295064000000	3.419789000000	0.083199000000
C	3.582604000000	1.070089000000	0.197802000000
C	4.009247000000	0.165956000000	1.177237000000
C	4.529210000000	1.796448000000	-0.531121000000
C	5.368864000000	-0.026971000000	1.403505000000
C	5.888462000000	1.602482000000	-0.300541000000
C	6.311046000000	0.686393000000	0.661972000000
H	3.280308000000	-0.389068000000	1.760524000000
H	4.204644000000	2.491373000000	-1.300096000000
H	5.692171000000	-0.734045000000	2.160278000000
H	6.616244000000	2.161152000000	-0.879858000000
H	7.370688000000	0.530251000000	0.835926000000
P			
Rh	-1.287662000000	0.893036000000	0.069957000000
Cl	-1.589353000000	0.640690000000	-2.288704000000
O	-3.394904000000	1.006515000000	0.438069000000
N	0.669099000000	0.916367000000	-0.172362000000

N	-0.679610000000	-1.317371000000	0.176920000000
C	2.777609000000	-0.130902000000	0.004798000000
N	0.622387000000	-1.377547000000	-0.268126000000
H	-3.092887000000	3.567142000000	-0.090799000000
C	0.661705000000	4.574134000000	-0.352813000000
C	0.291824000000	3.232008000000	-0.228341000000
C	3.297212000000	1.169693000000	-0.066727000000
C	-1.229003000000	-2.477816000000	-0.132981000000
N	2.574975000000	2.280558000000	-0.203697000000
C	1.390224000000	-0.211833000000	-0.154417000000
C	-0.328365000000	5.549657000000	-0.387697000000
C	-1.064434000000	2.851846000000	-0.131381000000
C	-0.299214000000	-3.291882000000	-0.820906000000
C	0.861498000000	-2.566841000000	-0.925122000000
C	-1.673637000000	5.179086000000	-0.295752000000
C	1.254517000000	2.131355000000	-0.199806000000
C	-2.044746000000	3.838129000000	-0.166694000000
Cl	-1.041639000000	1.113733000000	2.409695000000
H	-3.970707000000	0.419937000000	-0.077296000000
H	-3.570446000000	0.841938000000	1.374359000000
H	-0.058705000000	6.595742000000	-0.488566000000
H	-2.443337000000	5.944990000000	-0.324142000000
H	-0.470288000000	-4.276378000000	-1.230029000000
H	1.712310000000	4.838455000000	-0.425399000000
Cl	-4.703603000000	-0.564385000000	-2.131795000000
C	2.101397000000	-2.917863000000	-1.675565000000
H	2.855509000000	-3.370333000000	-1.027484000000
H	1.835380000000	-3.640525000000	-2.448401000000
H	2.543390000000	-2.043355000000	-2.157888000000
C	-2.648985000000	-2.772960000000	0.209611000000
H	-3.257291000000	-2.819272000000	-0.698101000000
H	-2.727152000000	-3.737944000000	0.716446000000
H	-3.053047000000	-1.997560000000	0.863249000000
H	-3.457308000000	-0.136169000000	-2.323923000000
H	4.371246000000	1.307049000000	0.026647000000
C	3.654285000000	-1.268220000000	0.367194000000
C	3.270435000000	-2.135092000000	1.397691000000
C	4.881374000000	-1.461866000000	-0.274489000000
C	4.093605000000	-3.195871000000	1.762516000000
C	5.705464000000	-2.521771000000	0.096430000000
C	5.311142000000	-3.393695000000	1.110578000000
H	2.326325000000	-1.982139000000	1.912457000000
H	5.180600000000	-0.801096000000	-1.082915000000
H	3.785472000000	-3.866409000000	2.558056000000
H	6.652096000000	-2.670376000000	-0.412778000000
H	5.951814000000	-4.222333000000	1.394614000000

Table S3. Optimized geometries of the ground state of rhodium(III) complexes with **HL^{2,5}** from Figure 4 in Cartesian (XYZ) coordinates as calculated in Gaussian at the ωB97XD/Stuttgart RSC 1997/6-31+g(d) level of theory **in the gas phase**.

R			
Rh	1.485633000000	0.799075000000	0.175140000000

Cl	1.979527000000	0.798927000000	-2.108007000000
O	-1.187257000000	-1.589126000000	2.577531000000
N	0.166540000000	-0.720865000000	-0.188555000000
N	-0.151756000000	1.797609000000	-0.178859000000
C	-2.123096000000	-1.318263000000	-0.313596000000
N	-1.259017000000	1.036500000000	-0.487005000000
H	4.874541000000	-1.284385000000	1.205986000000
C	2.457940000000	-3.294389000000	-1.063672000000
C	1.955532000000	-2.335922000000	-0.181777000000
C	-1.652543000000	-2.633270000000	-0.402556000000
C	-0.410205000000	3.059314000000	-0.471864000000
N	-0.374940000000	-2.988790000000	-0.422669000000
C	-1.114792000000	-0.353768000000	-0.335403000000
C	3.829600000000	-3.513327000000	-1.140156000000
C	2.834136000000	-1.632084000000	0.654004000000
C	-1.710427000000	3.124521000000	-1.014205000000
C	-2.214744000000	1.849851000000	-1.058001000000
C	4.705966000000	-2.783644000000	-0.337613000000
C	0.512978000000	-2.016858000000	-0.236532000000
C	4.206414000000	-1.850292000000	0.566063000000
Cl	0.910852000000	0.761065000000	2.496341000000
H	-0.525076000000	-0.879361000000	2.666413000000
H	-1.020245000000	-2.189687000000	3.307472000000
H	4.216538000000	-4.245028000000	-1.842070000000
H	5.776104000000	-2.945206000000	-0.416848000000
H	-2.199619000000	4.011403000000	-1.387167000000
H	1.773385000000	-3.842099000000	-1.702265000000
C	-3.483265000000	1.419066000000	-1.710938000000
H	-4.285233000000	1.240541000000	-0.992244000000
H	-3.793269000000	2.219175000000	-2.385400000000
H	-3.341245000000	0.511237000000	-2.299997000000
C	0.577541000000	4.153541000000	-0.288169000000
H	1.405263000000	4.026169000000	-0.991803000000
H	0.095257000000	5.117261000000	-0.458786000000
H	1.004757000000	4.121442000000	0.716328000000
H	-2.378968000000	-3.441769000000	-0.433504000000
C	-3.558044000000	-1.077823000000	-0.045623000000
C	-3.922968000000	-0.359645000000	1.098097000000
C	-4.547958000000	-1.610899000000	-0.875392000000
C	-5.268686000000	-0.141886000000	1.379700000000
C	-5.892515000000	-1.393114000000	-0.588849000000
C	-6.254417000000	-0.649736000000	0.533912000000
H	-3.151594000000	-0.001996000000	1.773421000000
H	-4.264808000000	-2.169219000000	-1.763876000000
H	-5.547018000000	0.415988000000	2.268075000000
H	-6.656436000000	-1.797111000000	-1.245501000000
H	-7.302920000000	-0.476013000000	0.754121000000
H	2.457005000000	-0.982374000000	1.444505000000
Cl	3.185133000000	2.300376000000	0.624409000000

TS1

Rh	-1.536820000000	-0.615525000000	0.005896000000
Cl	-1.320192000000	-0.881629000000	-2.329258000000
O	1.416973000000	-0.002867000000	2.811706000000

N	-0.108322000000	0.728064000000	-0.164351000000	
N	0.241315000000	-1.755847000000	0.178664000000	
C	2.162148000000	1.350981000000	-0.223660000000	
N	1.331554000000	-1.033238000000	-0.249109000000	
H	-4.869699000000	0.496353000000	0.133641000000	
C	-2.466925000000	3.501129000000	-0.288143000000	
C	-1.949935000000	2.205535000000	-0.255868000000	
C	1.663188000000	2.656786000000	-0.329636000000	
C	0.511034000000	-3.031777000000	-0.015687000000	
N	0.378930000000	2.997751000000	-0.388885000000	
C	1.177129000000	0.358637000000	-0.218872000000	
C	-3.836605000000	3.711867000000	-0.196435000000	
C	-2.807634000000	1.081246000000	-0.135515000000	
C	1.787633000000	-3.153467000000	-0.605102000000	
C	2.274754000000	-1.881790000000	-0.785352000000	
C	-4.683773000000	2.619938000000	-0.044551000000	
C	-0.497964000000	2.006556000000	-0.274197000000	
C	-4.175830000000	1.320141000000	-0.002828000000	
Cl	-1.673335000000	-0.382725000000	2.361924000000	
H	0.483314000000	-0.265497000000	2.711656000000	
H	1.407107000000	0.648614000000	3.517411000000	
H	-4.237810000000	4.719297000000	-0.226648000000	
H	-5.754571000000	2.769925000000	0.052009000000	
H	2.272780000000	-4.066022000000	-0.917214000000	
H	-1.773731000000	4.331972000000	-0.371020000000	
Cl	-3.515595000000	-2.018714000000	-0.010022000000	
C	3.500644000000	-1.485933000000	-1.536444000000	
H	4.340288000000	-1.251599000000	-0.879447000000	
H	3.783544000000	-2.324085000000	-2.175767000000	
H	3.311205000000	-0.620424000000	-2.174637000000	
C	-0.498254000000	-4.081107000000	0.296273000000	
H	-1.198551000000	-4.175277000000	-0.540010000000	
H	-0.012659000000	-5.044651000000	0.461110000000	
H	-1.073946000000	-3.804210000000	1.182039000000	
H	-3.159320000000	-0.421931000000	-0.308993000000	
H	2.376025000000	3.477986000000	-0.345418000000	
C	3.614074000000	1.141681000000	-0.013918000000	
C	4.058772000000	0.420124000000	1.099827000000	
C	4.543748000000	1.700461000000	-0.896201000000	
C	5.424260000000	0.245818000000	1.308672000000	
C	5.907749000000	1.520366000000	-0.683060000000	
C	6.349986000000	0.788247000000	0.417803000000	
H	3.328271000000	0.007972000000	1.791256000000	
H	4.198526000000	2.251486000000	-1.767062000000	
H	5.765136000000	-0.315021000000	2.173281000000	
H	6.623640000000	1.944768000000	-1.379838000000	
H	7.413110000000	0.644302000000	0.582841000000	

P

Rh	-1.297759000000	0.903927000000	0.052670000000	
Cl	-1.572806000000	0.589838000000	-2.299680000000	
O	-3.399451000000	1.039796000000	0.424944000000	
N	0.661438000000	0.920630000000	-0.161884000000	
N	-0.674751000000	-1.329941000000	0.190571000000	

C	2.768844000000	-0.127016000000	0.020641000000
N	0.618235000000	-1.373476000000	-0.269855000000
H	-3.093953000000	3.566315000000	-0.175029000000
C	0.666248000000	4.576617000000	-0.338879000000
C	0.290904000000	3.234960000000	-0.222440000000
C	3.288141000000	1.175549000000	-0.028838000000
C	-1.215824000000	-2.491501000000	-0.121194000000
N	2.571334000000	2.285511000000	-0.164611000000
C	1.382019000000	-0.203490000000	-0.145328000000
C	-0.321663000000	5.549527000000	-0.399912000000
C	-1.066134000000	2.854278000000	-0.157046000000
C	-0.287952000000	-3.290477000000	-0.830731000000
C	0.862183000000	-2.550584000000	-0.942686000000
C	-1.668627000000	5.176634000000	-0.343488000000
C	1.247867000000	2.138486000000	-0.177812000000
C	-2.045154000000	3.838883000000	-0.221798000000
Cl	-1.117991000000	1.106738000000	2.383656000000
H	-3.979297000000	0.436829000000	-0.070480000000
H	-3.506632000000	0.895185000000	1.375616000000
H	-0.051440000000	6.596156000000	-0.494200000000
H	-2.437396000000	5.942644000000	-0.394161000000
H	-0.455842000000	-4.270137000000	-1.252902000000
H	1.719843000000	4.834951000000	-0.383670000000
Cl	-4.631136000000	-0.614129000000	-1.997848000000
C	2.097065000000	-2.873774000000	-1.715199000000
H	2.865177000000	-3.335427000000	-1.089981000000
H	1.828964000000	-3.575059000000	-2.507457000000
H	2.525424000000	-1.982336000000	-2.179346000000
C	-2.628018000000	-2.798474000000	0.243733000000
H	-3.261923000000	-2.812825000000	-0.647515000000
H	-2.696863000000	-3.775159000000	0.730189000000
H	-3.008586000000	-2.038689000000	0.929677000000
H	-3.391713000000	-0.157077000000	-2.256571000000
H	4.361700000000	1.311942000000	0.081733000000
C	3.640577000000	-1.270352000000	0.374827000000
C	3.249920000000	-2.151169000000	1.390576000000
C	4.870980000000	-1.461413000000	-0.261053000000
C	4.066750000000	-3.220337000000	1.743112000000
C	5.690174000000	-2.528685000000	0.098209000000
C	5.286868000000	-3.414172000000	1.095888000000
H	2.304383000000	-1.998044000000	1.902942000000
H	5.176190000000	-0.788487000000	-1.057744000000
H	3.752734000000	-3.899975000000	2.528756000000
H	6.640120000000	-2.672316000000	-0.406684000000
H	5.923401000000	-4.248619000000	1.372475000000

Table S4. Optimized geometries of the ground state of rhodium(III) complexes with **HL[2,6]** from Figure S25 in Cartesian (XYZ) coordinates as calculated in Gaussian at the ωB97XD/Stuttgart RSC 1997/6-31+g(d) level of theory **in EtOH continuum solvation model**.

R			
Rh	-1.926434000000	0.396112000000	-0.259279000000
Cl	-1.554606000000	0.731982000000	-2.556008000000

O	0.657518000000	-1.291286000000	2.738376000000
N	0.089988000000	0.731795000000	0.008217000000
N	-1.235199000000	-1.423368000000	-0.365075000000
C	2.234318000000	-0.288678000000	-0.146941000000
N	0.126391000000	-1.543975000000	-0.239390000000
H	-2.512559000000	4.670881000000	2.036564000000
C	0.083283000000	4.161619000000	-0.797479000000
C	-0.116952000000	3.161571000000	0.159854000000
C	2.793977000000	0.983969000000	-0.044834000000
C	-1.755277000000	-2.642128000000	-0.424293000000
N	2.020075000000	2.077031000000	0.062207000000
C	0.855444000000	-0.368518000000	-0.107856000000
C	-0.669048000000	5.330239000000	-0.744772000000
C	-1.049243000000	3.349022000000	1.185005000000
C	-0.700784000000	-3.573614000000	-0.330668000000
C	4.256793000000	1.194961000000	-0.077809000000
C	0.471082000000	-2.872201000000	-0.201899000000
C	-1.608447000000	5.513646000000	0.271630000000
C	0.706598000000	1.930185000000	0.081602000000
C	-1.792188000000	4.527151000000	1.237991000000
C	6.139007000000	2.628220000000	-0.586893000000
C	5.142466000000	0.192181000000	0.337322000000
Cl	-2.242669000000	0.083817000000	2.076377000000
C	7.016732000000	1.624938000000	-0.174940000000
C	6.516253000000	0.409816000000	0.292029000000
H	1.194881000000	-0.629764000000	3.184195000000
H	-0.223432000000	-0.891025000000	2.662031000000
H	-0.522898000000	6.098757000000	-1.496696000000
H	-2.191430000000	6.428242000000	0.311597000000
H	4.077025000000	3.194842000000	-0.848783000000
H	6.526034000000	3.573819000000	-0.952439000000
H	8.088566000000	1.790877000000	-0.215141000000
H	7.195753000000	-0.367122000000	0.626314000000
H	4.767914000000	-0.749857000000	0.725868000000
H	-0.802445000000	-4.647865000000	-0.344362000000
C	4.765256000000	2.418879000000	-0.531913000000
H	0.818649000000	4.015482000000	-1.582274000000
Cl	-4.241192000000	0.241031000000	-0.615412000000
C	1.850624000000	-3.399596000000	-0.022603000000
H	2.314219000000	-2.984732000000	0.876353000000
H	1.787471000000	-4.481757000000	0.092252000000
H	2.482759000000	-3.189623000000	-0.889992000000
C	-3.208883000000	-2.921394000000	-0.552598000000
H	-3.612178000000	-2.458612000000	-1.455592000000
H	-3.366932000000	-3.999085000000	-0.595951000000
H	-3.751160000000	-2.508196000000	0.300969000000
H	2.850199000000	-1.158902000000	-0.297517000000
H	-1.187881000000	2.583417000000	1.941478000000

IM1

Rh	-1.946134000000	0.154873000000	-0.211415000000
Cl	-1.784465000000	-0.028579000000	-2.562874000000
O	0.486396000000	-1.571991000000	2.724842000000
N	0.107018000000	0.149168000000	-0.147885000000

N	-1.577083000000	-1.751954000000	-0.064368000000
C	2.038275000000	-1.228092000000	-0.287715000000
N	-0.257406000000	-2.107985000000	-0.197234000000
H	-1.874723000000	4.681186000000	-1.460273000000
H	-0.852356000000	2.449574000000	-1.757248000000
C	0.663206000000	3.361247000000	1.156461000000
C	0.302897000000	2.565866000000	0.064452000000
C	2.809165000000	-0.071664000000	-0.171280000000
C	-2.288812000000	-2.852847000000	0.131347000000
N	2.237399000000	1.138297000000	-0.045493000000
C	0.667509000000	-1.071323000000	-0.218975000000
C	0.088277000000	4.617700000000	1.316488000000
C	-0.604471000000	3.047728000000	-0.884688000000
C	-1.403459000000	-3.951332000000	0.133701000000
C	4.286919000000	-0.121980000000	-0.191036000000
C	-0.134119000000	-3.469174000000	-0.057340000000
C	-0.832502000000	5.092047000000	0.380634000000
C	0.918398000000	1.222539000000	-0.064266000000
C	-1.171911000000	4.310709000000	-0.721474000000
C	6.398857000000	0.964094000000	-0.658764000000
C	4.977991000000	-1.276823000000	0.198667000000
Cl	-2.039375000000	0.402209000000	2.138044000000
C	7.081177000000	-0.190901000000	-0.275846000000
C	6.368575000000	-1.308428000000	0.158038000000
H	1.226917000000	-1.012060000000	2.976361000000
H	-0.276779000000	-0.973931000000	2.677924000000
H	0.357992000000	5.227241000000	2.172736000000
H	-1.280592000000	6.071979000000	0.509562000000
H	4.473983000000	1.897695000000	-0.908263000000
H	6.949554000000	1.835801000000	-0.996793000000
H	8.165575000000	-0.219363000000	-0.312312000000
H	6.894712000000	-2.204242000000	0.470816000000
H	4.441953000000	-2.147196000000	0.563703000000
H	-1.676159000000	-4.986005000000	0.273547000000
C	5.009225000000	1.002638000000	-0.610801000000
H	1.379188000000	2.987696000000	1.881497000000
Cl	-4.272080000000	0.380851000000	-0.354971000000
C	1.145172000000	-4.227809000000	-0.091257000000
H	1.808761000000	-3.920987000000	0.722137000000
H	0.916999000000	-5.285465000000	0.040812000000
H	1.663262000000	-4.108972000000	-1.046534000000
C	-3.763532000000	-2.865972000000	0.312327000000
H	-4.263293000000	-2.596579000000	-0.621326000000
H	-4.081066000000	-3.864553000000	0.613191000000
H	-4.064467000000	-2.140620000000	1.070721000000
H	2.495552000000	-2.192710000000	-0.425865000000
TS1			
Rh	-1.815383000000	0.164518000000	-0.121915000000
Cl	-1.552809000000	0.349962000000	-2.467341000000
O	0.578500000000	-1.956699000000	2.760957000000
N	0.136559000000	0.052853000000	-0.008181000000
N	-1.448929000000	-1.902525000000	-0.263884000000
C	2.146756000000	-1.145687000000	-0.183825000000

N	-0.108022000000	-2.200041000000	-0.227251000000	
H	-3.304064000000	3.325760000000	0.402874000000	
H	-2.811026000000	1.516276000000	-0.235990000000	
C	0.553193000000	3.649593000000	0.367453000000	
C	-0.031595000000	2.398737000000	0.169465000000	
C	2.804719000000	0.085048000000	-0.068479000000	
C	-2.104378000000	-3.046836000000	-0.276218000000	
N	2.139644000000	1.249608000000	0.045200000000	
C	0.763496000000	-1.123790000000	-0.133584000000	
C	-0.241651000000	4.774606000000	0.556695000000	
C	-1.443503000000	2.246993000000	0.148937000000	
C	-1.177277000000	-4.115902000000	-0.238016000000	
C	4.282538000000	0.163126000000	-0.093548000000	
C	0.077587000000	-3.562423000000	-0.195049000000	
C	-1.624841000000	4.635252000000	0.570272000000	
C	0.820521000000	1.207383000000	0.056775000000	
C	-2.219885000000	3.385157000000	0.375775000000	
C	6.290131000000	1.410301000000	-0.614866000000	
C	5.071972000000	-0.906389000000	0.348387000000	
Cl	-2.041413000000	-0.067659000000	2.231876000000	
C	7.071508000000	0.340580000000	-0.176938000000	
C	6.460381000000	-0.814444000000	0.309838000000	
H	1.246244000000	-1.358543000000	3.109515000000	
H	-0.227826000000	-1.420302000000	2.695065000000	
H	0.215908000000	5.746122000000	0.707622000000	
H	-2.259049000000	5.500112000000	0.736486000000	
H	4.290605000000	2.154829000000	-0.907255000000	
H	6.762051000000	2.310093000000	-0.995784000000	
H	8.154160000000	0.409406000000	-0.211311000000	
H	7.064004000000	-1.643182000000	0.664961000000	
H	4.611719000000	-1.802302000000	0.753361000000	
H	-1.407442000000	-5.170459000000	-0.232528000000	
C	4.902554000000	1.326228000000	-0.567822000000	
H	1.635771000000	3.722776000000	0.384735000000	
Cl	-4.199904000000	0.699834000000	-0.352694000000	
C	1.401572000000	-4.235961000000	-0.101948000000	
H	1.954440000000	-3.892972000000	0.777103000000	
H	1.237528000000	-5.309210000000	-0.003938000000	
H	2.005885000000	-4.067080000000	-0.997724000000	
C	-3.593554000000	-3.082864000000	-0.314961000000	
H	-3.966720000000	-2.500767000000	-1.161379000000	
H	-3.945540000000	-4.110605000000	-0.407661000000	
H	-4.006420000000	-2.648715000000	0.600066000000	
H	2.695244000000	-2.060514000000	-0.335779000000	

IM2

Rh	1.810882000000	-0.174185000000	-0.078447000000	
Cl	1.848662000000	-0.245047000000	-2.449564000000	
O	-1.293742000000	-0.098297000000	2.979701000000	
N	-0.140212000000	-0.023711000000	-0.083507000000	
N	1.450581000000	2.015761000000	-0.138153000000	
C	-2.143534000000	1.196844000000	-0.198025000000	
N	0.097097000000	2.263349000000	-0.134124000000	
H	3.324423000000	-3.083880000000	0.054088000000	

H	4.386375000000	-0.443827000000	-1.431325000000
C	-0.523498000000	-3.661255000000	0.014269000000
C	-0.000528000000	-2.366134000000	-0.027429000000
C	-2.817025000000	-0.028132000000	-0.161782000000
C	2.049647000000	3.189006000000	-0.119147000000
N	-2.168821000000	-1.203839000000	-0.109854000000
C	-0.758189000000	1.163735000000	-0.135772000000
C	0.347021000000	-4.743457000000	0.068278000000
C	1.392071000000	-2.126964000000	-0.015576000000
C	1.083318000000	4.224384000000	-0.099127000000
C	-4.296854000000	-0.084691000000	-0.197899000000
C	-0.147474000000	3.621928000000	-0.106213000000
C	1.726390000000	-4.520224000000	0.080542000000
C	-0.848589000000	-1.174911000000	-0.079212000000
C	2.248304000000	-3.224537000000	0.039378000000
C	-6.318671000000	-1.269708000000	-0.805612000000
C	-5.075213000000	0.960897000000	0.314586000000
Cl	1.889222000000	-0.099109000000	2.298500000000
C	-7.088849000000	-0.223409000000	-0.296910000000
C	-6.464791000000	0.888497000000	0.267607000000
H	-1.576879000000	-1.016697000000	2.941827000000
H	-0.337896000000	-0.120176000000	2.810616000000
H	-0.043240000000	-5.755259000000	0.102641000000
H	2.407063000000	-5.365824000000	0.123295000000
H	-4.326558000000	-2.015876000000	-1.143967000000
H	-6.799863000000	-2.136839000000	-1.246250000000
H	-8.172221000000	-0.277170000000	-0.336696000000
H	-7.059160000000	1.698450000000	0.677645000000
H	-4.605087000000	1.821963000000	0.779463000000
H	1.270707000000	5.287399000000	-0.077574000000
C	-4.930131000000	-1.204847000000	-0.751067000000
H	-1.599497000000	-3.806352000000	0.005052000000
Cl	4.312665000000	-0.365882000000	-0.141943000000
C	-1.491273000000	4.266973000000	-0.082321000000
H	-2.087737000000	3.933794000000	0.771440000000
H	-1.349830000000	5.344459000000	0.007024000000
H	-2.048083000000	4.076880000000	-1.004488000000
C	3.537642000000	3.298929000000	-0.117514000000
H	3.959434000000	2.816472000000	-1.003268000000
H	3.838888000000	4.347307000000	-0.113738000000
H	3.957379000000	2.810735000000	0.766115000000
H	-2.686473000000	2.121313000000	-0.295130000000

TS2

Rh	-1.742930000000	0.176274000000	-0.032133000000
Cl	-1.687900000000	0.422966000000	-2.403798000000
O	0.784757000000	-1.716023000000	2.771914000000
N	0.190480000000	0.073884000000	-0.003590000000
N	-1.349029000000	-1.991633000000	-0.233470000000
C	2.216096000000	-1.082408000000	-0.270330000000
N	0.009092000000	-2.208395000000	-0.237841000000
H	-3.355924000000	2.988238000000	0.295819000000
H	-3.810926000000	0.520580000000	-1.933907000000
C	0.472878000000	3.711300000000	0.362281000000

C	-0.003242000000	2.405419000000	0.217864000000
C	2.863261000000	0.149360000000	-0.145847000000
C	-1.923796000000	-3.175413000000	-0.220914000000
N	2.189930000000	1.300642000000	0.033033000000
C	0.832711000000	-1.094119000000	-0.166360000000
C	-0.439708000000	4.752906000000	0.484158000000
C	-1.384796000000	2.123787000000	0.188241000000
C	-0.933400000000	-4.191431000000	-0.208894000000
C	4.338000000000	0.245060000000	-0.237482000000
C	0.282729000000	-3.562323000000	-0.209066000000
C	-1.811536000000	4.482541000000	0.459282000000
C	0.872689000000	1.242953000000	0.080669000000
C	-2.286356000000	3.176624000000	0.311870000000
C	6.306390000000	1.523341000000	-0.829807000000
C	5.158109000000	-0.827642000000	0.134760000000
Cl	-1.987299000000	-0.052162000000	2.306331000000
C	7.118051000000	0.449758000000	-0.462142000000
C	6.541773000000	-0.722864000000	0.025325000000
H	-0.064809000000	-1.249936000000	2.714751000000
H	1.421005000000	-1.039865000000	3.023725000000
H	-0.088635000000	5.773016000000	0.599130000000
H	-2.520485000000	5.299750000000	0.556848000000
H	4.287645000000	2.256440000000	-0.997733000000
H	6.750967000000	2.437303000000	-1.210140000000
H	8.196910000000	0.528183000000	-0.551367000000
H	7.169295000000	-1.555438000000	0.326009000000
H	4.725866000000	-1.738001000000	0.538464000000
H	-1.096966000000	-5.258435000000	-0.192324000000
C	4.923632000000	1.425441000000	-0.712416000000
H	1.542456000000	3.897032000000	0.378940000000
Cl	-4.753927000000	0.491130000000	-1.023619000000
C	1.642365000000	-4.169607000000	-0.163027000000
H	2.213639000000	-3.804215000000	0.694969000000
H	1.531786000000	-5.249616000000	-0.061367000000
H	2.207040000000	-3.975739000000	-1.079553000000
C	-3.407102000000	-3.310600000000	-0.211780000000
H	-3.878450000000	-2.326170000000	-0.240904000000
H	-3.741753000000	-3.890905000000	-1.075675000000
H	-3.733497000000	-3.834377000000	0.690734000000
H	2.774035000000	-1.981184000000	-0.470453000000
P			
Rh	-1.364633000000	0.886868000000	-0.150437000000
Cl	-1.300004000000	1.149693000000	-2.531586000000
O	-3.506195000000	1.051536000000	-0.106845000000
N	0.597999000000	0.829792000000	-0.120785000000
N	-0.881000000000	-1.287670000000	-0.347143000000
C	2.666587000000	-0.271392000000	-0.280556000000
N	0.484893000000	-1.459749000000	-0.315403000000
H	-3.038148000000	3.651567000000	0.130788000000
C	0.768173000000	4.473777000000	0.223574000000
C	0.328000000000	3.153614000000	0.092175000000
C	3.272231000000	0.983803000000	-0.156364000000
C	-1.412618000000	-2.492864000000	-0.341882000000

N	2.560538000000	2.116975000000	-0.027436000000
C	1.279659000000	-0.316276000000	-0.238575000000
C	-0.170492000000	5.494407000000	0.325003000000
C	-1.048086000000	2.836927000000	0.059631000000
C	-0.391285000000	-3.473595000000	-0.310393000000
C	4.747231000000	1.121986000000	-0.186054000000
C	0.803756000000	-2.803334000000	-0.288173000000
C	-1.534850000000	5.189541000000	0.291793000000
C	1.242388000000	2.014798000000	-0.022720000000
C	-1.975215000000	3.870285000000	0.158957000000
C	6.699619000000	2.448660000000	-0.723471000000
C	5.583023000000	0.088903000000	0.256748000000
Cl	-1.497370000000	0.620950000000	2.194119000000
C	7.527250000000	1.414768000000	-0.284500000000
C	6.966432000000	0.237910000000	0.210563000000
H	-3.989526000000	0.549992000000	-0.781918000000
H	-3.823347000000	0.750621000000	0.755696000000
H	0.154650000000	6.524293000000	0.430073000000
H	-2.265229000000	5.990062000000	0.369266000000
H	4.667992000000	3.107264000000	-1.007923000000
H	7.132201000000	3.365274000000	-1.111233000000
H	8.605956000000	1.528062000000	-0.325114000000
H	7.605991000000	-0.563208000000	0.566432000000
H	5.161799000000	-0.823560000000	0.667522000000
H	-0.520452000000	-4.545527000000	-0.298856000000
C	5.316822000000	2.307043000000	-0.668582000000
H	1.832934000000	4.685716000000	0.246881000000
Cl	-4.310440000000	-0.191536000000	-3.056165000000
C	2.180231000000	-3.373851000000	-0.232496000000
H	2.734549000000	-3.012090000000	0.637759000000
H	2.095267000000	-4.457763000000	-0.150056000000
H	2.750824000000	-3.149612000000	-1.138359000000
C	-2.892110000000	-2.683664000000	-0.342318000000
H	-3.353110000000	-2.129532000000	-1.163831000000
H	-3.138116000000	-3.740610000000	-0.452726000000
H	-3.321810000000	-2.322368000000	0.596725000000
H	3.260991000000	-1.155079000000	-0.438511000000
H	-3.078205000000	0.312025000000	-2.976658000000

Table S5. Optimized geometries of the ground state of rhodium(III) complexes with **HL^{2,6}** from Figure S25 in Cartesian (XYZ) coordinates as calculated in Gaussian at the ωB97XD/Stuttgart RSC 1997/6-31+g(d) level of theory **in the gas phase**.

R			
Rh	-1.870511000000	0.501816000000	0.003201000000
Cl	-1.725218000000	1.029298000000	-2.262326000000
O	0.926978000000	-1.544848000000	2.664011000000
N	0.161801000000	0.783391000000	0.097597000000
N	-1.223350000000	-1.311209000000	-0.298483000000
C	2.279051000000	-0.255963000000	-0.119399000000
N	0.133148000000	-1.479059000000	-0.172631000000
H	-2.981456000000	4.323393000000	1.518571000000
C	0.180191000000	4.229288000000	-0.724092000000

C	-0.091183000000	3.175724000000	0.150255000000
C	2.848171000000	1.015650000000	-0.036569000000
C	-1.780291000000	-2.502296000000	-0.427617000000
N	2.093085000000	2.121366000000	0.057402000000
C	0.899369000000	-0.323088000000	-0.046608000000
C	-0.698922000000	5.303990000000	-0.803777000000
C	-1.224934000000	3.220919000000	0.972748000000
C	-0.753983000000	-3.473963000000	-0.378744000000
C	4.316123000000	1.206890000000	-0.081539000000
C	0.436185000000	-2.816354000000	-0.202664000000
C	-1.844224000000	5.336261000000	-0.008410000000
C	0.778606000000	1.980157000000	0.119790000000
C	-2.100267000000	4.301066000000	0.886398000000
C	6.214457000000	2.607659000000	-0.615217000000
C	5.191882000000	0.200333000000	0.342074000000
Cl	-1.899886000000	-0.009841000000	2.341502000000
C	7.081764000000	1.598059000000	-0.200020000000
C	6.568010000000	0.396768000000	0.285183000000
H	1.234438000000	-1.431370000000	3.566423000000
H	0.042450000000	-1.135139000000	2.645526000000
H	-0.499173000000	6.109857000000	-1.502589000000
H	-2.536438000000	6.168438000000	-0.086829000000
H	4.154821000000	3.200216000000	-0.859299000000
H	6.611528000000	3.545428000000	-0.990331000000
H	8.155487000000	1.749514000000	-0.248936000000
H	7.239435000000	-0.384132000000	0.627431000000
H	4.803871000000	-0.727541000000	0.752015000000
H	-0.888531000000	-4.542708000000	-0.444414000000
C	4.838750000000	2.417912000000	-0.549278000000
H	1.058052000000	4.184221000000	-1.359721000000
Cl	-4.173547000000	0.475982000000	-0.077076000000
C	1.800267000000	-3.379969000000	-0.010998000000
H	2.235603000000	-2.990596000000	0.914051000000
H	1.715233000000	-4.463853000000	0.076889000000
H	2.460453000000	-3.162023000000	-0.856235000000
C	-3.246218000000	-2.698778000000	-0.568313000000
H	-3.640044000000	-2.067874000000	-1.368663000000
H	-3.458679000000	-3.747688000000	-0.780273000000
H	-3.753059000000	-2.399266000000	0.353232000000
H	2.885967000000	-1.133636000000	-0.265501000000
H	-1.397824000000	2.450784000000	1.721072000000

TS1

Rh	-1.800232000000	0.174815000000	-0.178048000000
Cl	-1.459268000000	0.356254000000	-2.500911000000
O	0.520498000000	-1.996783000000	2.631830000000
N	0.152621000000	0.062817000000	-0.038068000000
N	-1.433234000000	-1.890117000000	-0.321375000000
C	2.161303000000	-1.132210000000	-0.214421000000
N	-0.096971000000	-2.188542000000	-0.238222000000
H	-3.296487000000	3.277463000000	0.491704000000
H	-2.736236000000	1.549353000000	-0.357321000000
C	0.554776000000	3.651050000000	0.377212000000
C	-0.024405000000	2.405182000000	0.139896000000

C	2.815659000000	0.101331000000	-0.115989000000
C	-2.094281000000	-3.027325000000	-0.301265000000
N	2.153724000000	1.265232000000	-0.011676000000
C	0.777845000000	-1.109731000000	-0.156057000000
C	-0.245197000000	4.760235000000	0.624527000000
C	-1.435787000000	2.243904000000	0.136159000000
C	-1.172976000000	-4.098994000000	-0.193688000000
C	4.295371000000	0.179319000000	-0.150090000000
C	0.080805000000	-3.546351000000	-0.135471000000
C	-1.626154000000	4.606325000000	0.667709000000
C	0.831847000000	1.220032000000	0.011072000000
C	-2.215339000000	3.361287000000	0.436939000000
C	6.299130000000	1.412073000000	-0.712255000000
C	5.088534000000	-0.875068000000	0.317039000000
Cl	-2.063575000000	-0.116285000000	2.167753000000
C	7.083993000000	0.356003000000	-0.251047000000
C	6.476386000000	-0.784935000000	0.269557000000
H	0.863601000000	-1.789877000000	3.504266000000
H	-0.306402000000	-1.485305000000	2.561671000000
H	0.207160000000	5.729781000000	0.803780000000
H	-2.262787000000	5.457515000000	0.888846000000
H	4.293537000000	2.146652000000	-1.008905000000
H	6.768442000000	2.302585000000	-1.117838000000
H	8.166511000000	0.425064000000	-0.292257000000
H	7.082996000000	-1.602388000000	0.645950000000
H	4.626997000000	-1.756625000000	0.752327000000
H	-1.407641000000	-5.151175000000	-0.138135000000
C	4.912308000000	1.328710000000	-0.656398000000
H	1.637396000000	3.727098000000	0.385445000000
Cl	-4.154126000000	0.704058000000	-0.468054000000
C	1.398591000000	-4.207838000000	0.069531000000
H	1.888992000000	-3.797048000000	0.957341000000
H	1.232658000000	-5.273660000000	0.231679000000
H	2.055767000000	-4.098731000000	-0.798692000000
C	-3.582921000000	-3.041888000000	-0.361127000000
H	-3.932081000000	-2.460087000000	-1.217882000000
H	-3.954583000000	-4.064356000000	-0.444223000000
H	-3.994732000000	-2.582170000000	0.542325000000
H	2.711927000000	-2.047362000000	-0.357592000000
P			
Rh	-1.373681000000	0.898843000000	-0.190692000000
Cl	-1.259646000000	1.163703000000	-2.561996000000
O	-3.507558000000	1.089667000000	-0.163702000000
N	0.588469000000	0.827035000000	-0.122639000000
N	-0.884195000000	-1.295989000000	-0.395841000000
C	2.657058000000	-0.270911000000	-0.302806000000
N	0.477172000000	-1.461672000000	-0.343345000000
H	-3.036037000000	3.654777000000	0.100526000000
C	0.770598000000	4.462863000000	0.278273000000
C	0.326022000000	3.147226000000	0.115123000000
C	3.263256000000	0.984289000000	-0.164170000000
C	-1.414058000000	-2.498887000000	-0.355690000000
N	2.555748000000	2.111945000000	-0.017886000000

C	1.270019000000	-0.312640000000	-0.255996000000
C	-0.164931000000	5.482255000000	0.383893000000
C	-1.049453000000	2.835636000000	0.056545000000
C	-0.391501000000	-3.476865000000	-0.281915000000
C	4.739246000000	1.122182000000	-0.203483000000
C	0.799698000000	-2.800347000000	-0.266289000000
C	-1.529477000000	5.181287000000	0.319955000000
C	1.233601000000	2.013275000000	-0.010595000000
C	-1.974186000000	3.869688000000	0.155684000000
C	6.684931000000	2.457391000000	-0.736085000000
C	5.580613000000	0.083747000000	0.212079000000
Cl	-1.614353000000	0.550472000000	2.121546000000
C	7.517638000000	1.416593000000	-0.327097000000
C	6.962978000000	0.231875000000	0.153418000000
H	-3.984670000000	0.602873000000	-0.857155000000
H	-3.775368000000	0.757887000000	0.705208000000
H	0.160019000000	6.509297000000	0.514787000000
H	-2.258124000000	5.983537000000	0.398286000000
H	4.646319000000	3.120583000000	-0.978364000000
H	7.113268000000	3.381868000000	-1.109881000000
H	8.595873000000	1.531082000000	-0.377842000000
H	7.607134000000	-0.574025000000	0.490383000000
H	5.161107000000	-0.832946000000	0.616517000000
H	-0.517238000000	-4.548306000000	-0.233180000000
C	5.303392000000	2.315423000000	-0.668232000000
H	1.836393000000	4.664811000000	0.324575000000
Cl	-4.216242000000	-0.220001000000	-2.986298000000
C	2.177315000000	-3.365052000000	-0.162967000000
H	2.715520000000	-2.965928000000	0.701888000000
H	2.094581000000	-4.445517000000	-0.036548000000
H	2.766667000000	-3.178585000000	-1.065994000000
C	-2.893993000000	-2.684716000000	-0.353243000000
H	-3.345372000000	-2.208188000000	-1.227478000000
H	-3.147190000000	-3.746406000000	-0.363642000000
H	-3.320999000000	-2.233869000000	0.548041000000
H	3.251017000000	-1.150285000000	-0.485371000000
H	-2.981636000000	0.322857000000	-2.953666000000

Table S6. Optimized geometry of the **S$_0$ state** of the **[RhL^{2,5}(H$_2$O)Cl$_2$]** complex (geometry **a** in Figure 7) in Cartesian (XYZ) coordinates as calculated in Gaussian at the B3LYP/Stuttgart RSC 1997/6-31+g(d) level of theory **in the gas phase**.

Rh	1.583789000000	0.710307000000	0.174608000000
Cl	1.725807000000	1.189853000000	-2.163735000000
O	3.132131000000	2.106507000000	0.666659000000
N	0.232589000000	-0.680783000000	-0.182187000000
N	-0.414711000000	1.837142000000	0.232124000000
C	-2.002833000000	-1.438872000000	-0.135702000000
N	-1.354370000000	0.975579000000	-0.289059000000
H	4.756674000000	0.104599000000	0.136611000000
C	2.836045000000	-3.251607000000	-0.339530000000
C	2.140649000000	-2.047014000000	-0.201733000000
C	-1.444773000000	-2.721986000000	-0.229701000000

C	-0.835060000000	3.056596000000	-0.052028000000
N	-0.142996000000	-2.990561000000	-0.317180000000
C	-1.075223000000	-0.394739000000	-0.213566000000
C	4.226038000000	-3.239036000000	-0.310182000000
C	2.822706000000	-0.823163000000	-0.027529000000
C	-2.035122000000	2.999622000000	-0.798390000000
C	-2.334855000000	1.670792000000	-0.966233000000
C	4.907375000000	-2.029539000000	-0.141572000000
C	0.681637000000	-1.951634000000	-0.236575000000
C	4.213462000000	-0.825074000000	0.000883000000
Cl	1.459456000000	0.293179000000	2.497140000000
H	3.146151000000	2.947091000000	0.182463000000
H	3.096378000000	2.311901000000	1.610627000000
H	4.781354000000	-4.164605000000	-0.420335000000
H	5.993361000000	-2.025024000000	-0.119978000000
H	-2.592920000000	3.831023000000	-1.202758000000
H	2.286225000000	-4.178439000000	-0.472141000000
C	-3.422699000000	1.069907000000	-1.790406000000
H	-4.304171000000	0.831967000000	-1.190560000000
H	-3.711526000000	1.797135000000	-2.550668000000
H	-3.092823000000	0.157868000000	-2.292526000000
C	-0.059160000000	4.256308000000	0.371645000000
H	0.378295000000	4.753031000000	-0.499000000000
H	-0.710593000000	4.974051000000	0.876291000000
H	0.744643000000	3.970114000000	1.052635000000
H	-2.108610000000	-3.581928000000	-0.198795000000
C	-3.442498000000	-1.269238000000	0.167567000000
C	-3.833064000000	-0.424164000000	1.213531000000
C	-4.414868000000	-1.976250000000	-0.546321000000
C	-5.180942000000	-0.270831000000	1.522838000000
C	-5.763055000000	-1.824412000000	-0.230979000000
C	-6.149069000000	-0.967755000000	0.799249000000
H	-3.083092000000	0.116219000000	1.783838000000
H	-4.120787000000	-2.624242000000	-1.366887000000
H	-5.475073000000	0.390838000000	2.331004000000
H	-6.511980000000	-2.369855000000	-0.795860000000
H	-7.200274000000	-0.846276000000	1.040057000000

Table S7. Optimized **geometry in the vicinity of S_0/T_1 crossing point** of the **[RhL^{2,5}(H$_2$O)Cl$_2$]** complex in Cartesian (XYZ) coordinates as calculated in Gaussian at the B3LYP/Stuttgart RSC 1997/6-31+g(d) level of theory **in the gas phase**.

Rh	-1.573050000000	-0.531387000000	0.095614000000
Cl	-2.562480000000	-1.768735000000	-1.657301000000
O	-4.929790000000	-1.821266000000	0.706456000000
N	0.006091000000	0.796007000000	-0.314132000000
N	0.535174000000	-1.777016000000	0.119792000000
C	2.291470000000	1.436258000000	-0.119931000000
N	1.518381000000	-0.939697000000	-0.379850000000
H	-4.622531000000	0.404061000000	0.234556000000
C	-2.416790000000	3.564175000000	-0.401263000000
C	-1.822181000000	2.295444000000	-0.278819000000
C	1.805595000000	2.753964000000	-0.241166000000
C	0.904050000000	-3.007626000000	-0.203210000000

N	0.518860000000	3.095617000000	-0.371068000000
C	1.301767000000	0.445598000000	-0.273118000000
C	-3.802212000000	3.682987000000	-0.323794000000
C	-2.627387000000	1.141523000000	-0.072731000000
C	2.111208000000	-2.984194000000	-0.950752000000
C	2.477046000000	-1.661934000000	-1.076220000000
C	-4.590023000000	2.546402000000	-0.102127000000
C	-0.375008000000	2.098684000000	-0.327709000000
C	-4.011395000000	1.276876000000	0.031508000000
Cl	-1.925693000000	-0.769671000000	2.385067000000
H	-4.600337000000	-2.205704000000	-0.105668000000
H	-4.561500000000	-2.363459000000	1.421527000000
H	-4.270007000000	4.658198000000	-0.424279000000
H	-5.670059000000	2.645181000000	-0.021588000000
H	2.631712000000	-3.826881000000	-1.384852000000
H	-1.783914000000	4.432219000000	-0.551247000000
C	3.602292000000	-1.083336000000	-1.871180000000
H	4.517366000000	-0.989572000000	-1.281253000000
H	3.808312000000	-1.745532000000	-2.713795000000
H	3.358686000000	-0.096790000000	-2.268596000000
C	0.078379000000	-4.189138000000	0.194328000000
H	-0.315687000000	-4.689600000000	-0.687988000000
H	0.680899000000	-4.904316000000	0.754247000000
H	-0.754117000000	-3.866023000000	0.810590000000
H	2.511710000000	3.580352000000	-0.193577000000
C	3.697462000000	1.144536000000	0.265643000000
C	3.937765000000	0.302153000000	1.368275000000
C	4.793748000000	1.673096000000	-0.438102000000
C	5.241309000000	-0.042832000000	1.726247000000
C	6.099215000000	1.320025000000	-0.082571000000
C	6.326262000000	0.450537000000	0.991165000000
H	3.098186000000	-0.083256000000	1.942381000000
H	4.626269000000	2.319852000000	-1.297358000000
H	5.406178000000	-0.700571000000	2.576551000000
H	6.938218000000	1.704755000000	-0.658306000000
H	7.340121000000	0.158952000000	1.252325000000

Table S8. Optimized geometry of the **T$_1$ state** of the **[RhL^{2,5}(H$_2$O)Cl$_2$]** complex (geometry **b** in Figure 7) in Cartesian (XYZ) coordinates as calculated in Gaussian at the B3LYP/Stuttgart RSC 1997/6-31+g(d) level of theory **in the gas phase**.

Rh	-1.278022000000	0.797515000000	0.108586000000
Cl	-2.763053000000	0.585874000000	-1.722797000000
O	-5.098114000000	2.227061000000	0.311645000000
N	0.768000000000	0.793097000000	-0.204985000000
N	-0.559439000000	-1.447423000000	0.203868000000
C	2.905895000000	-0.230478000000	-0.034692000000
N	0.744855000000	-1.507231000000	-0.268800000000
H	-3.021670000000	3.523839000000	0.041274000000
C	0.756799000000	4.470040000000	-0.288994000000
C	0.369812000000	3.121467000000	-0.193826000000
C	3.399213000000	1.091896000000	-0.121451000000
C	-1.122845000000	-2.606444000000	-0.109535000000

N	2.662791000000	2.194969000000	-0.236841000000
C	1.508955000000	-0.328911000000	-0.174365000000
C	-0.217715000000	5.462886000000	-0.271630000000
C	-1.002969000000	2.765256000000	-0.068961000000
C	-0.202333000000	-3.421054000000	-0.821799000000
C	0.966140000000	-2.702929000000	-0.939590000000
C	-1.570285000000	5.110220000000	-0.156078000000
C	1.333485000000	2.029957000000	-0.214123000000
C	-1.968420000000	3.770699000000	-0.052666000000
Cl	-2.415700000000	0.920913000000	2.157656000000
H	-4.740916000000	1.743369000000	-0.448175000000
H	-4.608145000000	1.868334000000	1.066693000000
H	0.068475000000	6.507461000000	-0.347964000000
H	-2.329735000000	5.887725000000	-0.143889000000
H	-0.386362000000	-4.401481000000	-1.237440000000
H	1.811226000000	4.713763000000	-0.376919000000
C	2.194360000000	-3.057090000000	-1.714681000000
H	2.992350000000	-3.448501000000	-1.078828000000
H	1.930214000000	-3.826656000000	-2.443785000000
H	2.591955000000	-2.196572000000	-2.260187000000
C	-2.547440000000	-2.887262000000	0.243296000000
H	-3.177689000000	-2.819648000000	-0.650552000000
H	-2.652907000000	-3.894438000000	0.658165000000
H	-2.911058000000	-2.158412000000	0.970272000000
H	4.474051000000	1.245807000000	-0.051307000000
C	3.832619000000	-1.333338000000	0.321528000000
C	3.524214000000	-2.205241000000	1.381152000000
C	5.068086000000	-1.473304000000	-0.333353000000
C	4.424316000000	-3.201067000000	1.762852000000
C	5.968016000000	-2.469100000000	0.052151000000
C	5.647959000000	-3.338074000000	1.099214000000
H	2.584596000000	-2.095546000000	1.914807000000
H	5.317499000000	-0.814833000000	-1.160985000000
H	4.173193000000	-3.863598000000	2.585901000000
H	6.915786000000	-2.568008000000	-0.468840000000
H	6.347438000000	-4.112699000000	1.398883000000

Table S9. Optimized geometry of the **S$_4$ state** of the **[RhL^{2,5}(H$_2$O)Cl$_2$]** complex (geometry **c** in Figure X) in Cartesian (XYZ) coordinates as calculated in Gaussian at the B3LYP/Stuttgart RSC 1997/6-31+g(d) level of theory **in the gas phase**.

Rh	1.619454000000	0.664115000000	0.174130000000
Cl	1.774826000000	1.121102000000	-2.090748000000
O	3.290505000000	2.107019000000	0.448689000000
N	0.191076000000	-0.720125000000	-0.029915000000
N	-0.355190000000	1.865404000000	0.284507000000
C	-2.094983000000	-1.394552000000	-0.112294000000
N	-1.333231000000	1.029047000000	-0.251905000000
H	4.784183000000	-0.111507000000	0.104739000000
C	2.697946000000	-3.383927000000	-0.282628000000
C	2.053857000000	-2.147740000000	-0.154192000000
C	-1.577884000000	-2.690351000000	-0.183448000000
C	-0.738021000000	3.117692000000	-0.008403000000
N	-0.255622000000	-3.018738000000	-0.280287000000

|			
C	-1.137635000000	-0.345552000000	-0.145199000000
C	4.094153000000	-3.436742000000	-0.275553000000
C	2.806304000000	-0.959138000000	-0.011806000000
C	-1.941594000000	3.106783000000	-0.728715000000
C	-2.290742000000	1.773911000000	-0.917428000000
C	4.836478000000	-2.259851000000	-0.138130000000
C	0.589619000000	-2.001090000000	-0.166338000000
C	4.195432000000	-1.017106000000	-0.003878000000
Cl	1.669467000000	0.516278000000	2.514320000000
H	3.242966000000	2.827766000000	-0.196256000000
H	3.242431000000	2.490482000000	1.337754000000
H	4.601415000000	-4.391697000000	-0.376021000000
H	5.922782000000	-2.302717000000	-0.133633000000
H	-2.481191000000	3.961376000000	-1.111720000000
H	2.096189000000	-4.281956000000	-0.384645000000
C	-3.364908000000	1.217012000000	-1.793898000000
H	-4.273166000000	0.948144000000	-1.247989000000
H	-3.628557000000	1.972717000000	-2.539186000000
H	-3.020215000000	0.323263000000	-2.323645000000
C	0.102305000000	4.290109000000	0.393930000000
H	0.944645000000	4.431509000000	-0.295933000000
H	-0.489457000000	5.208837000000	0.377850000000
H	0.502149000000	4.159340000000	1.404013000000
H	-2.263161000000	-3.529836000000	-0.110590000000
C	-3.542394000000	-1.212531000000	0.159702000000
C	-3.972792000000	-0.356285000000	1.190150000000
C	-4.508373000000	-1.942910000000	-0.554535000000
C	-5.329840000000	-0.230743000000	1.489755000000
C	-5.865716000000	-1.818805000000	-0.251071000000
C	-6.282991000000	-0.959148000000	0.769623000000
H	-3.238983000000	0.201406000000	1.764589000000
H	-4.193323000000	-2.595800000000	-1.363653000000
H	-5.642886000000	0.431380000000	2.292174000000
H	-6.597308000000	-2.387988000000	-0.817740000000
H	-7.338974000000	-0.859166000000	1.003305000000

Cytotoxic activity
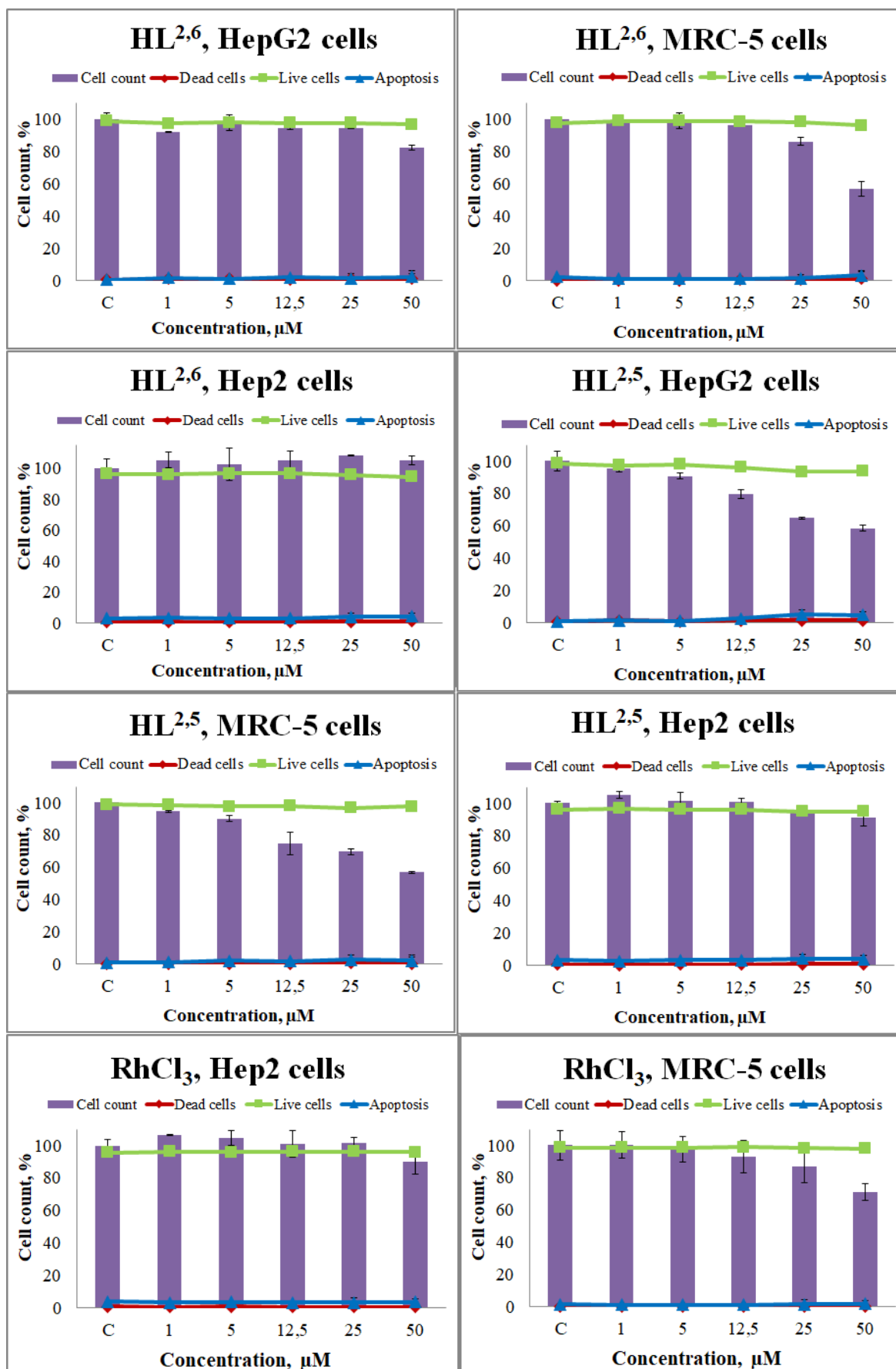
Figure S29. Effect of **HL^{2,6}**, **HL^{2,5}** and RhCl$_3$ on the viability of Hep2, HepG2 and MRC-5 cells determined by dual staining with Hoechst 33342/propidium iodide.