Electronic Supplementary Material (ESI) for New Journal of Chemistry.

Structural and solution equilibrium studies on half-sandwich organorhodium complexes of (N,N) donor bidentate ligands

János P. Mészáros,[a] Orsolya Dömötör,[a] Carmen M. Hackl,[b] Alexander Roller,[b] Bernhard K. Keppler,[b,c] Wolfgang Kandioller[b,c] and Éva A. Enyedy[a,*]

[a] Department of Inorganic and Analytical Chemistry, University of Szeged, Dóm tér 7, H-6720 Szeged, Hungary. E-mail: enyedy@chem.u-szeged.hu

[b] Institute of Inorganic Chemistry, Faculty of Chemistry, University of Vienna, Waehringer Str. 42, A-1090 Vienna, Austria.

[c] Research Cluster Translational Cancer Therapy Research, University of Vienna, Waehringer Str. 42, A-1090 Vienna, Austria.

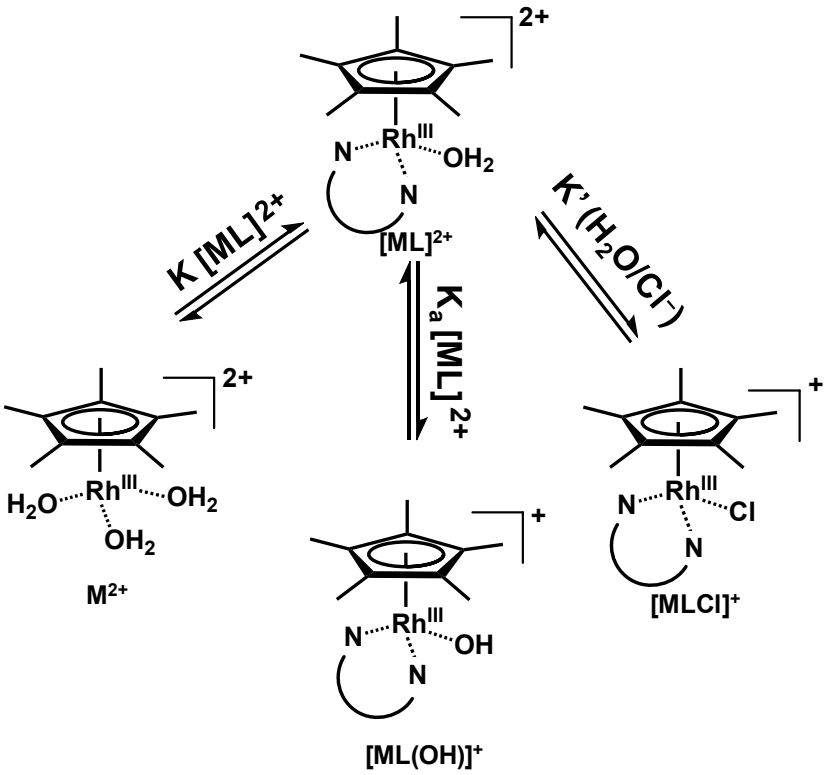

Chart S1. Complex formation and co-ligand exchange equilibrium processes for the $[Rh(\eta^5\text{-}C_5Me_5)(L)(H_2O)]^{2+}$ species

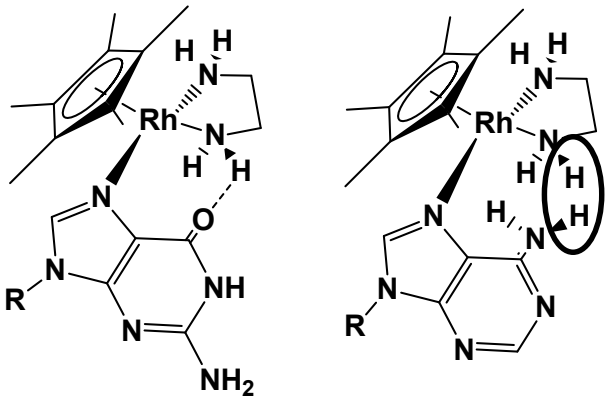

Chart S2. Proposed chemical structures of $[Rh(\eta^5\text{-}C_5Me_5)(en)(guanosine)]^{2+}$ and $[Rh(\eta^5\text{-}C_5Me_5)(en)(adenosine)]^{2+}$ based on the Ru(II)-arene analogues reported in Ref. [1]

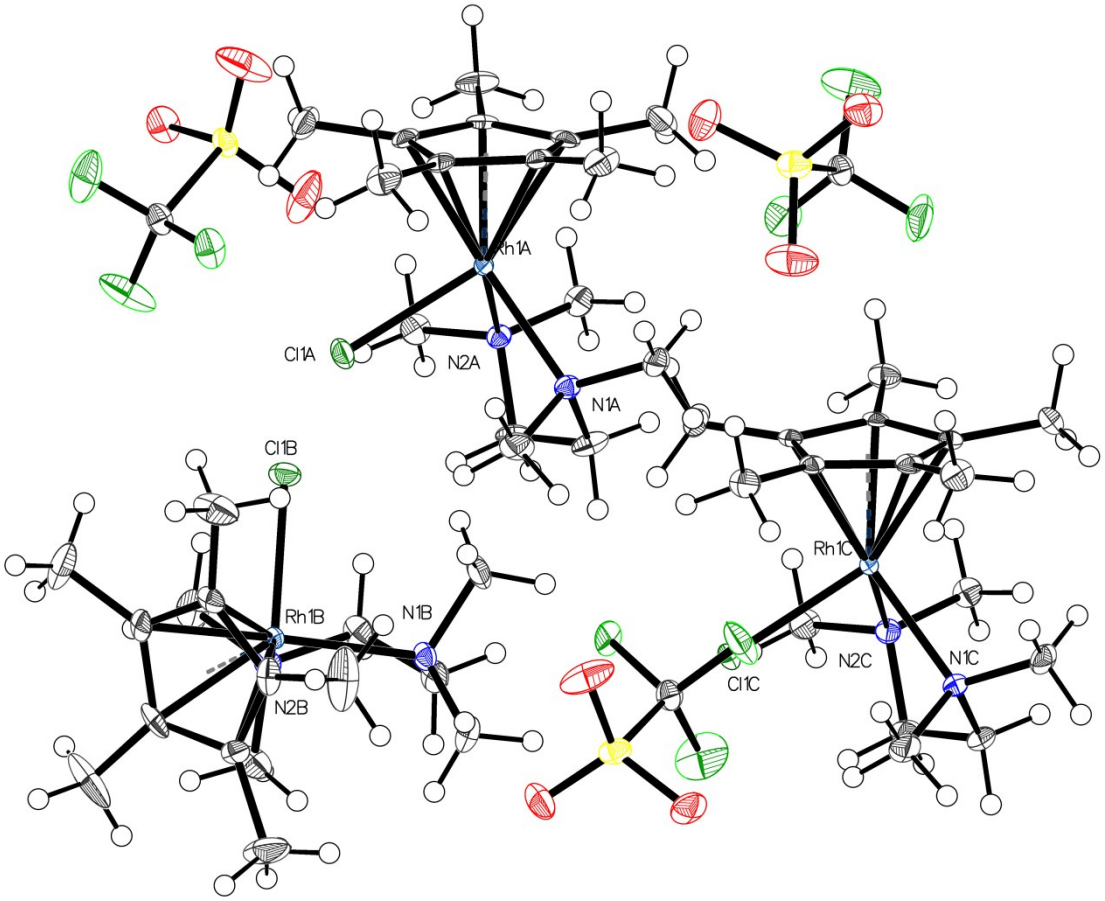

Fig. S1 Asymmetric unit of **2**, drawn with 50% displacement ellipsoids. Counter ion disorder and solvent water omitted for clarity.

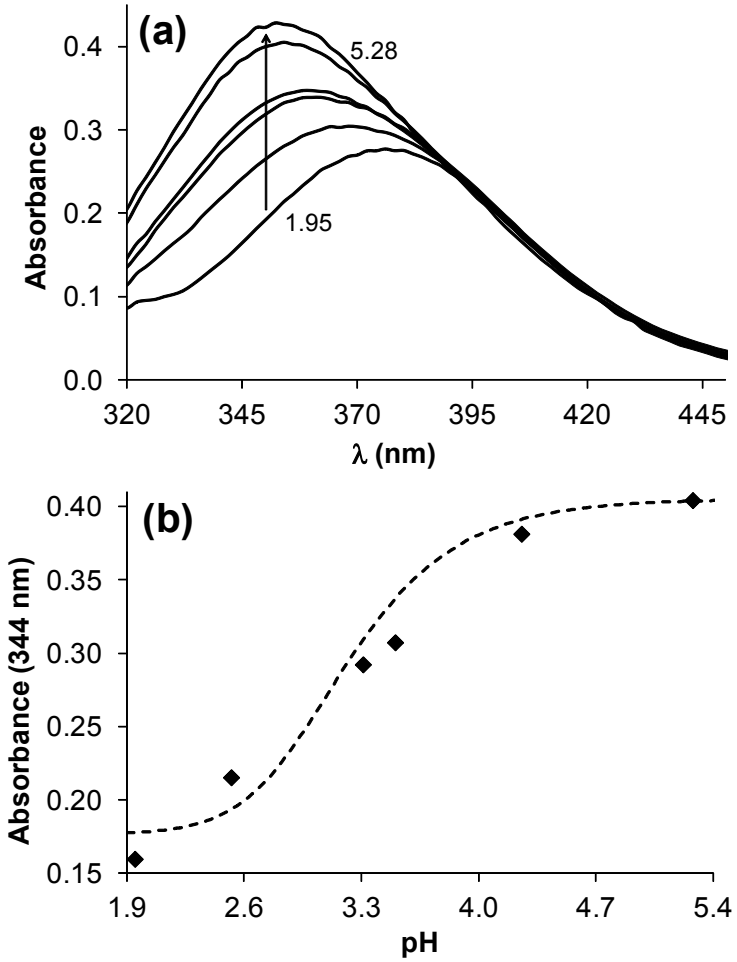

Fig. S2 UV–Vis spectra recorded for the $[Rh(\eta^5\text{-}C_5Me_5)(H_2O)_3]^{2+}$ – dmen (1:1) system ($c_{Rh} = c_{dmen} = 191\ \mu M$) at various pH values (pH = 2.0-5.3) (a). Absorbance values at 344 nm, dashed line shows calculated absorbance (b) {*T = 25 °C; I = 0.20 M (KNO_3); l = 1 cm*}.

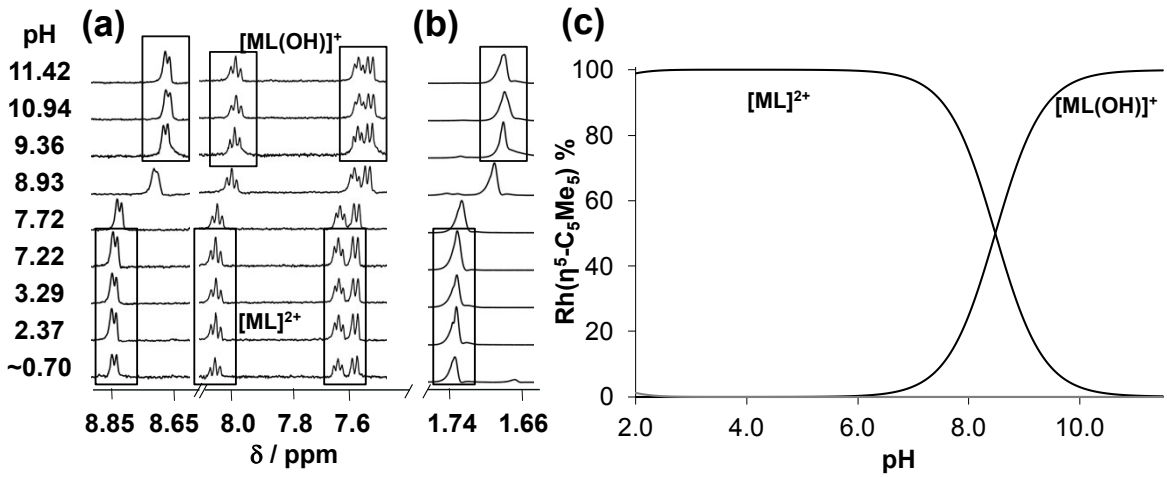

Fig. S3 ^{1}H NMR spectra for the $[Rh(\eta^5\text{-}C_5Me_5)(H_2O)_3]^{2+}$ – pin (1:1) system recorded at the indicated pH values: aromatic region (a); peaks of $C_5Me_5^-$ (b) {c_{Rh} = c_{pin} = *1 mM; T = 25 °C; I = 0.20 M (KNO_3); 10% D_2O*}. Concentration distribution curves for the $[Rh(\eta^5\text{-}C_5Me_5)(H_2O)_3]^{2+}$ – pin (1:1) systems calculated on the basis of the stability constants determined {c_{Rh} = c_L = *1 mM; T = 25 °C; I = 0.20 M (KNO_3)*} (c).

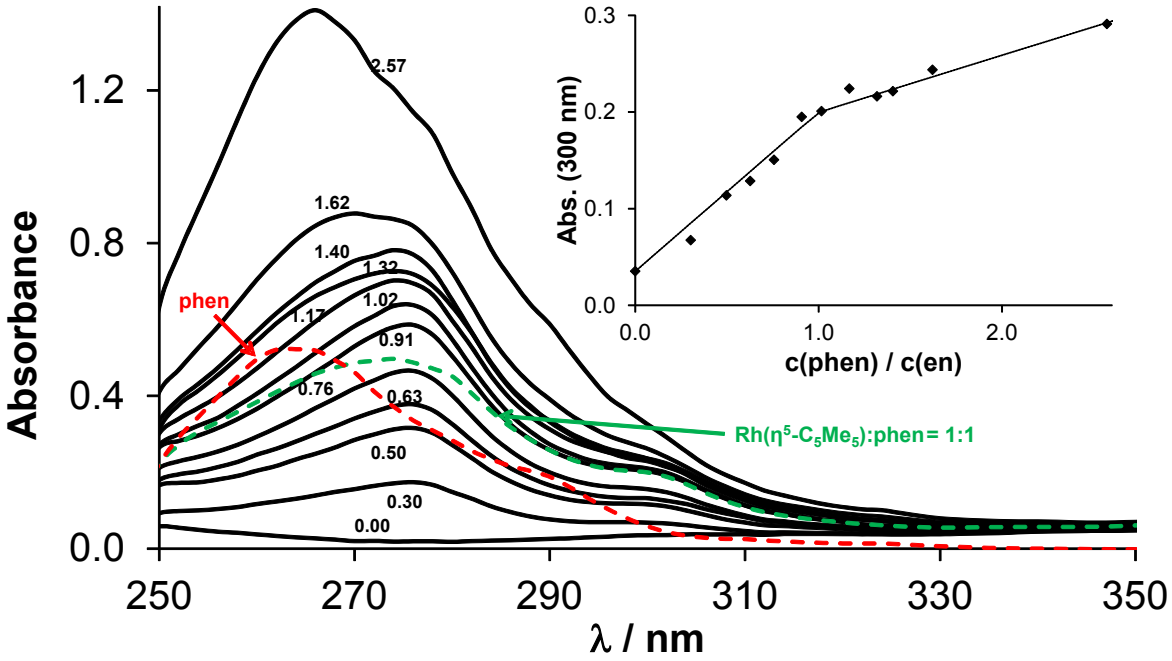

Fig. S4 UV-vis spectra for the displacement study of $[Rh(\eta^5\text{-}C_5Me_5)(en)(H_2O)]^{2+}$ – phen (1:1) system. The numbers show the different c(phen)-to-c(en) ratios. The spectra of $[Rh(\eta^5\text{-}C_5Me_5)(en)(H_2O)]^{2+}$ and phen are shown with dashed lines. Inset shows the absorbance value at 300 nm plotted against the phen:en ratio {$c_{Rh} = c_{en} = 50$ μM; I = 0.20 M KNO_3; pH = 5.69; T = 25 °C; l = 1 cm}

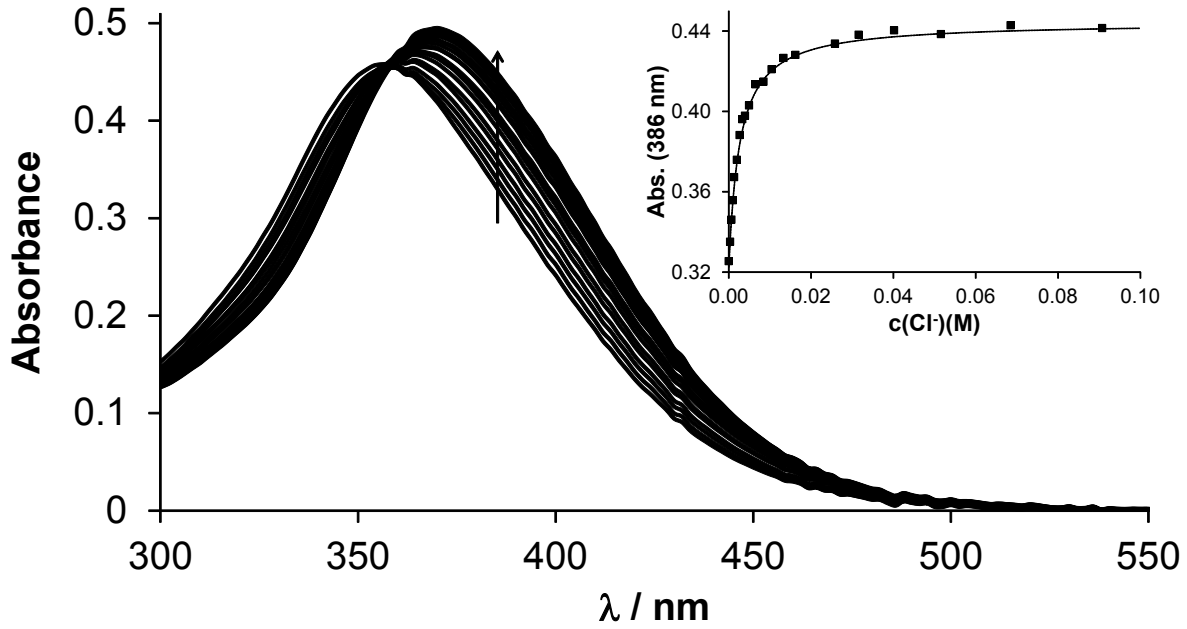

Fig. S5 UV–vis spectra recorded for $[Rh(\eta^5\text{-}C_5Me_5)(dmen)(H_2O)]^{2+}$ at various chloride ion concentrations. Inset shows absorbance values at 386 nm {$c_{Rh} = c_{dmen} = 200\ \mu M$; $c_{Cl^-} = 0.00\text{-}0.10$ M; $T = 25\ ^{\circ}C$; $pH = 7.40$; $l = 1$ cm}.

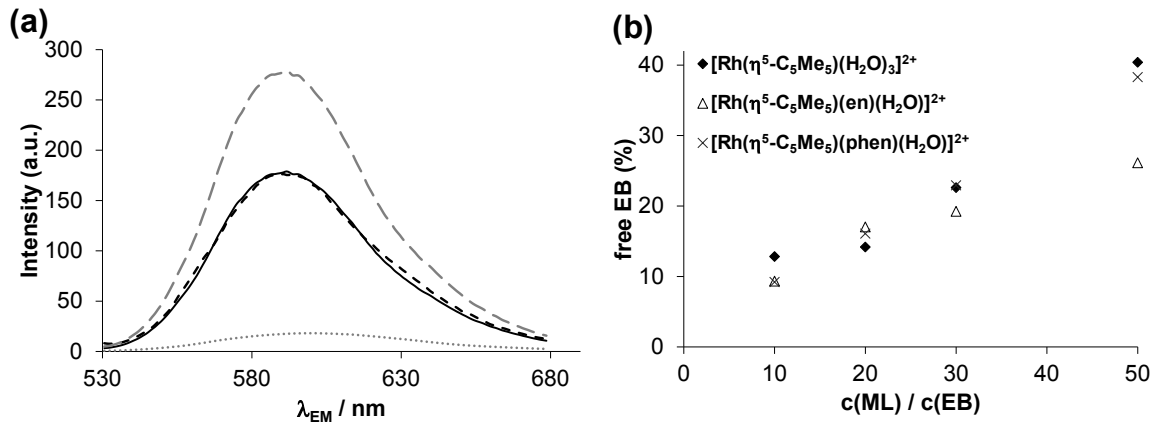

Fig. S6 Emission spectra of free ethidium bromide (grey dotted line), of 4:1 DNA nucleotide-to-ethidium bromide ratio (grey dashed line), of the 4:1:50 DNA nucleotide-to-EB-to-[Rh(η^5-C_5Me_5)(phen)(H_2O)]$^{2+}$ ternary system (black dashed line) and the calculated spectrum of the ternary system (black solid line) {c_{EB} = 5 μM; $c_{nucleotide}$ = 20 μM; c_{Rh} = c_{phen} = 250 μM; λ_{EX} = 510 nm; pH = 7.40 (20 mM phosphate); T = 25 °C; t = 24 h} (a). Percentage of the free EB in the function of the metal ion-to EB or complex-to-EB concentration ratio {c_{Rh} = c_L = 50-250 μM} (b).

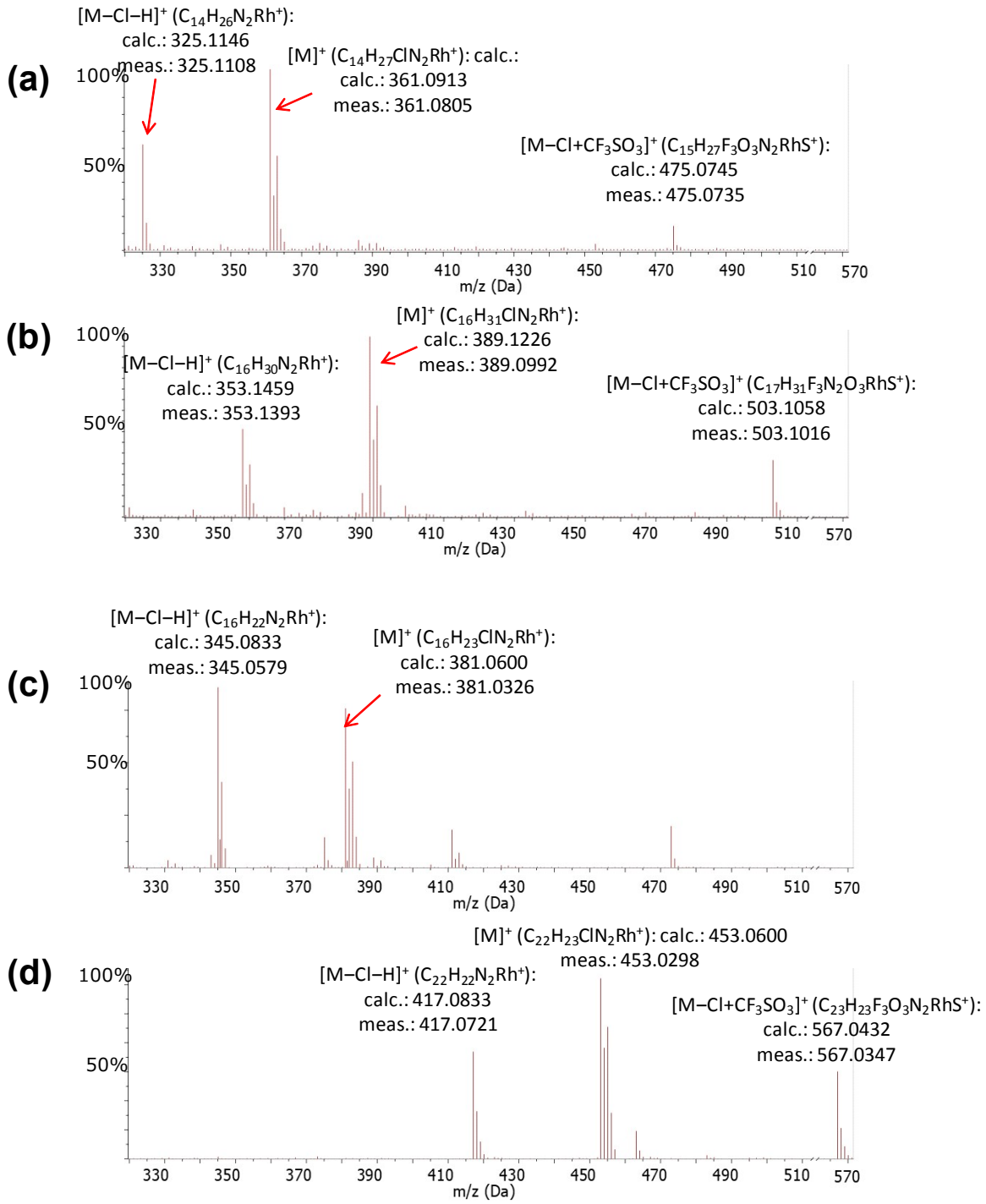

Fig. S7 ESI-MS of complexes **1** (a), **2** (b), **3** (c) and **4** (d) calculated and measured m/z values.

Table S1

Crystal data, data collection parameters and structure refinement details for complexes $[Rh(\eta^5\text{-}C_5Me_5)(L)Cl]^+$ of dmen (**1**), tmeda (**2**) and pin (**3**).[a]

Compound	**1**·CF_3SO_3	**2**·CF_3SO_3	**3**·Cl
CCDC number	1590516	1590517	1590518
Empirical formula	$C_{15}H_{27}ClF_3N_2O_3RhS$ [b]	$C_{51}H_{97}Cl_3F_9N_6O_{11}Rh_3S_3$ [c]	$C_{33}H_{50}Cl_4N_4ORh_2$ [d]
Formula weight	510.80	1652.6	866.39
Space group	$P2_12_12_1$	$P\ 1\ 2_1/n\ 1$	$P\ 1\ 2_1/n\ 1$
Crystal size / mm^3	0.380 × 0.280 × 0.266	0.355 × 0.296 × 0.242	0.247 × 0.260 × 0.349
Crystal habit	clear orange block	clear orange block	clear orange block
Crystal system	orthorhombic	monoclinic	monoclinic
a / Å	8.5159(3)	13.0112(4)	8.6742(3)
b / Å	9.7262(4)	37.6730(11)	14.5573(6)
c / Å	24.5900(10)	13.6054(4)	14.6705(6)
α / deg	90	90	90
β / deg	90	91.5748(9)	104.1107(13)
γ / deg	90	90	90
V / $Å^3$	2036.72(14)	6666.5(3)	1796.59(12)
Z	4	4	2
λ [Å]	0.71073	0.71073	0.71073
ρ_{calcd} / g/cm^3	1.666	1.647	1.602
Temperature / K	100	100	100
Absorption coefficient / mm^{-1}	1.116	1.031	1.248
F(000)	1040	3392	884
θ range for data collection	4.504 – 60.262°	3.184 – 50.7°	4.002 – 60.22°
Index ranges	−12 ≤ h ≤ 12	−15 ≤ h ≤ 15	−12 ≤ h ≤ 12
	−13 ≤ k ≤ 13	−41 ≤ k ≤ 45	−20 ≤ k ≤ 20
	−34 ≤ l ≤ 34	−16 ≤ l ≤ 16	−20 ≤ l ≤ 20
Reflections collected / unique	77632 / 5994	41099 / 12198	53397 / 5288
Data/restraints / parameters	5994 / 0 / 242	12198 / 15 / 918	5288 / 2 / 215
R(int)	0.0271	0.0407	0.0327
Goodness-of-fit on F^2 [e]	1.097	1.038	1.075
Final R indices [I>2σ(I)][f]			
R_1	0.0135	0.0298	0.0192
wR_2	0.0340	0.0603	0.0474

[a] Uncertainties (SD) of the last digits are shown in parentheses.
[b] $(C_{14}H_{27}ClN_2Rh)(CF_3SO_3)$
[c] $(C_{16}H_{31}ClN_2Rh)_3(CF_3SO_3)_3 \times 2\ H_2O$
[d] $(C_{16}H_{23}ClN_2Rh)_2Cl_2 \times CH_3OH$
[e] GOF = $\{\Sigma[w(F_o^2 - F_c^2)^2]/(n-p)\}^{1/2}$, where n is the number of reflections and p is the total number of parameters refined.
[f] $R_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$; $wR_2 = \{\Sigma[w(F_o^2 - F_c^2)^2]/\Sigma[w(F_o^2)^2]\}^{1/2}$

Table S2

pK_a [ML] values of the Rh(η^5-C_5Me_5) complexes formed with bidentate ligands in chloride-free aqueous solutions and H_2O/Cl^- exchange constants (logK') used in linear regression calculation {T = 25 °C; I = 0.2 M (KNO_3)}

	pK_a [ML]	logK' (H_2O/Cl^-)	Ref.
dhp	10.67	0.78	[2]
pic	9.32	2.20	[2]
6-Me-pic	9.49	2.10	[3]
HQ	10.27	1.81	[4]
HQS	10.10	1.54	[4]
PHQ	10.08	1.61	[4]
QA	9.31	2.33	[3]
3-iQA	9.26	2.06	[3]
en	9.58	2.14	[5]
dmen	8.505[a]	2.60	this work
pin	8.48	2.43	this work
bpy	8.61	2.58	[5]
phen	8.68	2.92	this work

[a] Average of the pK_a values of two isomers.

Table S3

Selected equilibrium constants (pK_a [ML], logK' (H_2O/Cl^-)), bond lengths, angles and torsion angles for complexes used in multilinear regression calculation

	maltol	**allomaltol**	**dhp**	**thiomaltol**	**pic**	**6-Me-pic**	**QA**	**HQ**	**bpy**	**phen**
Distances (Å)										
Rh-ring centroid	1.740	1.744	1.749	1.774	1.775	1.766	1.766	1.768	1.774	1.780
Rh-X	2.113	2.109	2.103	2.228	2.113	2.130	2.117	2.108	2.139	2.111
Rh-Cl	2.399	2.425	2.436	2.422	2.404	2.396	2.399	2.417	2.380	2.406
Angles (°)										
X-Rh-Y	78.55	78.85	79.71	82.85	77.70	76.97	77.29	78.36	75.30	77.68
X-Rh-Cl	87.50	86.98	87.56	90.11	86.85	69.57	88.44	88.63	86.30	86.38
Torsion angles (°)										
Methyl group–ring plane	2.461	2.192	2.082	2.956	3.304	2.988	3.340	1.982	4.578	3.21
X-C-C-Y	4.10	3.21	2.49	3.590	4.03	2.01	2.21	1.11	0.00	0.24
Ref.	[6,7]	[6,7]	[2]	[8]	[2,7]	[3]	[3]	[4]	[5,9]	[9]
logK' (H_2O/Cl^-) [a]	1.17	1.38	0.78	0.95	2.20	2.1	2.33	1.81	2.58	2.92

[a] For the references see Table S2.

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