Electronic Supplementary Material (ESI) for Faraday Discussions.

Supporting Information

Comparison of Halogen Bonding networks with Ru(II) complexes and analysis of the influence of the XB interaction on their reactivity

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Single-Crystal X-ray Structure Determination: 2a, 1b and 2b molecular structure figures and tables for all the compounds described

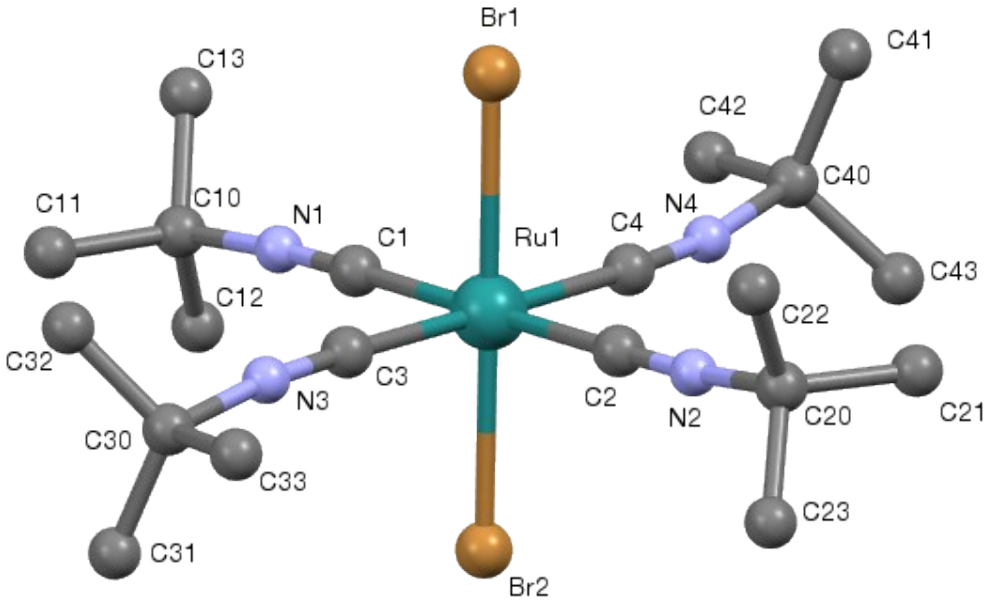

Figure S1. Molecular structure of **2a.**

Table S1. Bond lengths [Å] and angles [deg] for **2b**.

Ru(1)-C(2)#1	1.989(4)
Ru(1)-C(2)	1.989(4)
Ru(1)-C(1)#1	1.994(4)
Ru(1)-C(1)	1.994(4)
Ru(1)-Br(1)	2.5538(6)
Ru(1)-Br(1)#1	2.5538(6)
C(1)-N(1)	1.146(5)
C(2)-N(2)	1.151(5)
N(2)-C(20)	1.444(5)
C(20)-C(21)	1.488(7)
C(20)-C(22)	1.499(7)
C(20)-C(23)	1.528(7)
C(10)-N(1)	1.444(5)
C(10)-C(11)	1.458(7)
C(10)-C(13)	1.492(7)

C(10)-C(12)	1.531(8)

C(2)#1-Ru(1)-C(2)	180.0(3)
C(2)#1-Ru(1)-C(1)#1	90.52(15)
C(2)-Ru(1)-C(1)#1	89.48(15)
C(2)#1-Ru(1)-C(1)	89.48(15)
C(2)-Ru(1)-C(1)	90.52(15)
C(1)#1-Ru(1)-C(1)	180.0(3)
C(2)#1-Ru(1)-Br(1)	91.57(14)
C(2)-Ru(1)-Br(1)	88.43(14)
C(1)#1-Ru(1)-Br(1)	90.84(14)
C(1)-Ru(1)-Br(1)	89.16(14)
C(2)#1-Ru(1)-Br(1)#1	88.43(14)
C(2)-Ru(1)-Br(1)#1	91.57(14)
C(1)#1-Ru(1)-Br(1)#1	89.16(14)
C(1)-Ru(1)-Br(1)#1	90.84(14)
Br(1)-Ru(1)-Br(1)#1	180.00(3)
N(1)-C(1)-Ru(1)	179.1(5)
N(2)-C(2)-Ru(1)	177.0(4)
C(2)-N(2)-C(20)	172.3(5)
N(2)-C(20)-C(21)	108.8(4)
N(2)-C(20)-C(22)	109.7(4)
C(21)-C(20)-C(22)	113.3(5)
N(2)-C(20)-C(23)	106.1(4)
C(21)-C(20)-C(23)	109.1(5)
C(22)-C(20)-C(23)	109.7(5)
N(1)-C(10)-C(11)	110.6(4)
N(1)-C(10)-C(13)	108.4(4)
C(11)-C(10)-C(13)	113.0(6)
N(1)-C(10)-C(12)	105.0(4)
C(11)-C(10)-C(12)	111.2(5)
C(13)-C(10)-C(12)	108.3(6)
C(1)-N(1)-C(10)	175.0(5)

Symmetry transformations used to generate equivalent atoms: #1 -x,-y,-z

Table S2. Bond lengths [Å] and angles [deg] for **$(2a \cdot 2Br_2)_n$**.

Ru(1)-C(1)#1	1.997(10)
Ru(1)-C(1)#2	1.997(10)
Ru(1)-C(1)	1.997(10)
Ru(1)-C(1)#3	1.997(10)
Ru(1)-Br(2)#2	2.4940(18)
Ru(1)-Br(2)	2.4940(18)
Br(3)-Br(3)#4	2.369(3)
N(1)-C(1)	1.128(14)
N(1)-C(10)	1.462(16)
C(10)-C(11)	1.448(14)
C(10)-C(11)#5	1.448(14)
C(10)-C(12)	1.77(4)
C(1)#1-Ru(1)-C(1)#2	92.3(6)
C(1)#1-Ru(1)-C(1)	87.7(6)
C(1)#2-Ru(1)-C(1)	180.0(6)
C(1)#1-Ru(1)-C(1)#3	180.0(6)
C(1)#2-Ru(1)-C(1)#3	87.7(6)
C(1)-Ru(1)-C(1)#3	92.3(6)
C(1)#1-Ru(1)-Br(2)#2	90.0
C(1)#2-Ru(1)-Br(2)#2	90.0
C(1)-Ru(1)-Br(2)#2	90.0
C(1)#3-Ru(1)-Br(2)#2	90.0
C(1)#1-Ru(1)-Br(2)	90.0
C(1)#2-Ru(1)-Br(2)	90.0
C(1)-Ru(1)-Br(2)	90.0
C(1)#3-Ru(1)-Br(2)	90.0
Br(2)#2-Ru(1)-Br(2)	180.00(8)
C(1)-N(1)-C(10)	177.5(18)
N(1)-C(1)-Ru(1)	178.1(11)
N(1)-C(10)-C(11)	111.6(9)
N(1)-C(10)-C(11)#5	111.6(9)
C(11)-C(10)-C(11)#5	122.9(16)
N(1)-C(10)-C(12)	104.2(17)
C(11)-C(10)-C(12)	101.8(13)
C(11)#5-C(10)-C(12)	101.8(13)

Symmetry transformations used to generate equivalent atoms:
#1 x,y,-z #2 -x,-y,-z #3 -x,-y,z #4 -x-1,-y,-z #5 -y,-x,z

Table S3. Bond lengths [Å] and angles [deg] for **$(2a \cdot 3I_2)_n$**.

Ru(1)-C(1)	1.996(8)
Ru(1)-C(1)#1	1.996(8)
Ru(1)-C(11)	1.997(8)
Ru(1)-C(11)#1	1.997(8)
Ru(1)-Br(1)#1	2.5450(8)
Ru(1)-Br(1)	2.5450(8)
I(1)-I(1)#2	2.7025(12)
I(2)-I(3)	2.6491(11)
N(1)-C(1)	1.160(11)
N(1)-C(2)	1.465(11)
N(2)-C(11)	1.154(11)
N(2)-C(12)	1.465(10)
C(2)-C(4)	1.469(16)
C(2)-C(3)	1.529(14)
C(2)-C(5)	1.546(17)
C(12)-C(15)	1.509(13)
C(12)-C(13)	1.517(13)
C(12)-C(14)	1.533(14)
C(1)-Ru(1)-C(1)#1	180.0(6)
C(1)-Ru(1)-C(11)	94.0(3)
C(1)#1-Ru(1)-C(11)	86.0(3)
C(1)-Ru(1)-C(11)#1	86.0(3)
C(1)#1-Ru(1)-C(11)#1	94.0(3)
C(11)-Ru(1)-C(11)#1	180.0(5)
C(1)-Ru(1)-Br(1)#1	88.5(3)
C(1)#1-Ru(1)-Br(1)#1	91.5(3)
C(11)-Ru(1)-Br(1)#1	88.1(2)
C(11)#1-Ru(1)-Br(1)#1	91.9(2)
C(1)-Ru(1)-Br(1)	91.5(3)
C(1)#1-Ru(1)-Br(1)	88.5(3)
C(11)-Ru(1)-Br(1)	91.9(2)
C(11)#1-Ru(1)-Br(1)	88.1(2)
Br(1)#1-Ru(1)-Br(1)	180.00(4)
C(1)-N(1)-C(2)	175.8(9)
C(11)-N(2)-C(12)	175.0(8)
N(1)-C(1)-Ru(1)	175.8(7)
N(1)-C(2)-C(4)	108.7(8)
N(1)-C(2)-C(3)	106.5(7)
C(4)-C(2)-C(3)	111.4(10)
N(1)-C(2)-C(5)	106.5(9)
C(4)-C(2)-C(5)	113.8(11)
C(3)-C(2)-C(5)	109.6(10)
N(2)-C(11)-Ru(1)	174.6(7)

N(2)-C(12)-C(15)	108.3(7)
N(2)-C(12)-C(13)	107.5(7)
C(15)-C(12)-C(13)	111.0(8)
N(2)-C(12)-C(14)	106.8(7)
C(15)-C(12)-C(14)	112.0(8)
C(13)-C(12)-C(14)	111.2(8)

Symmetry transformations used to generate equivalent atoms:
#1 -x,-y,-z #2 -x,-y+1,-z

Table S4. Bond lengths [Å] and angles [deg] for **(3a·3I_2)$_n$**.

Ru(1)-C(11)	1.996(11)
Ru(1)-C(11)#1	1.996(11)
Ru(1)-C(21)#1	2.009(11)
Ru(1)-C(21)	2.009(11)
Ru(1)-I(1)	2.6140(10)
Ru(1)-I(1)#1	2.6140(10)
I(2)-I(2)#2	2.7178(15)
I(3)-I(4)	2.7289(13)
N(1)-C(11)	1.171(14)
N(1)-C(12)	1.435(14)
N(2)-C(21)	1.138(14)
N(2)-C(22)	1.488(14)
C(12)-C(15)	1.46(3)
C(12)-C(13)	1.50(2)
C(12)-C(14)	1.49(2)
C(22)-C(24)	1.455(19)
C(22)-C(25)	1.491(18)
C(22)-C(23)	1.517(18)

C(11)-Ru(1)-C(11)#1	180.0(11)
C(11)-Ru(1)-C(21)#1	91.7(4)
C(11)#1-Ru(1)-C(21)#1	88.3(4)
C(11)-Ru(1)-C(21)	88.3(4)
C(11)#1-Ru(1)-C(21)	91.7(4)
C(21)#1-Ru(1)-C(21)	180.0(7)
C(11)-Ru(1)-I(1)	90.4(3)
C(11)#1-Ru(1)-I(1)	89.6(3)
C(21)#1-Ru(1)-I(1)	86.4(3)
C(21)-Ru(1)-I(1)	93.6(3)
C(11)-Ru(1)-I(1)#1	89.6(3)
C(11)#1-Ru(1)-I(1)#1	90.4(3)
C(21)#1-Ru(1)-I(1)#1	93.6(3)

C(21)-Ru(1)-I(1)#1	86.4(3)
I(1)-Ru(1)-I(1)#1	180.00(4)
C(11)-N(1)-C(12)	175.4(12)
C(21)-N(2)-C(22)	173.7(10)
N(1)-C(11)-Ru(1)	174.8(10)
N(1)-C(12)-C(15)	104.2(12)
N(1)-C(12)-C(13)	109.8(12)
C(15)-C(12)-C(13)	117(2)
N(1)-C(12)-C(14)	107.4(12)
C(15)-C(12)-C(14)	105.2(17)
C(13)-C(12)-C(14)	112.6(18)
N(2)-C(21)-Ru(1)	177.1(10)
C(24)-C(22)-N(2)	107.4(11)
C(24)-C(22)-C(25)	108.1(12)
N(2)-C(22)-C(25)	108.0(10)
C(24)-C(22)-C(23)	112.2(12)
N(2)-C(22)-C(23)	108.5(9)
C(25)-C(22)-C(23)	112.5(12)

Symmetry transformations used to generate equivalent atoms:
#1 -x+2,-y,-z #2 -x+1,-y,-z

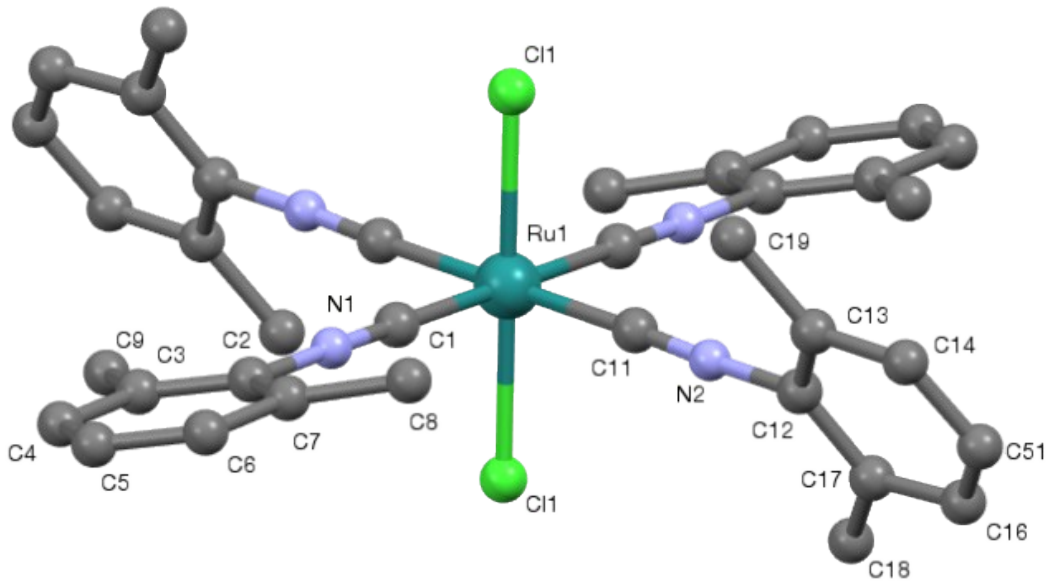

Figure S2. Molecular structure of **1b.**

Table S5. Bond lengths [Å] and angles [deg] for **1b**.

Ru(1)-C(1)#1	1.988(3)
Ru(1)-C(1)#2	1.988(3)
Ru(1)-C(1)	1.988(3)
Ru(1)-C(1)#3	1.988(3)
Ru(1)-Cl(1)	2.405(5)
Ru(1)-Cl(2)	2.416(4)
N(1)-C(1)	1.148(4)
N(1)-C(2)	1.398(4)
C(2)-C(7)	1.391(7)
C(2)-C(3)	1.388(6)
C(3)-C(4)	1.404(9)
C(3)-C(9)	1.486(9)
C(4)-C(5)	1.356(12)
C(5)-C(6)	1.349(11)
C(6)-C(7)	1.373(7)
C(7)-C(8)	1.483(8)
C(1)#1-Ru(1)-C(1)#2	178.7(4)
C(1)#1-Ru(1)-C(1)	89.992(8)
C(1)#2-Ru(1)-C(1)	89.992(6)
C(1)#1-Ru(1)-C(1)#3	89.992(7)
C(1)#2-Ru(1)-C(1)#3	89.992(7)
C(1)-Ru(1)-C(1)#3	178.7(4)
C(1)#1-Ru(1)-Cl(1)	90.7(2)
C(1)#2-Ru(1)-Cl(1)	90.7(2)
C(1)-Ru(1)-Cl(1)	90.7(2)
C(1)#3-Ru(1)-Cl(1)	90.7(2)
C(1)#1-Ru(1)-Cl(2)	89.3(2)
C(1)#2-Ru(1)-Cl(2)	89.3(2)
C(1)-Ru(1)-Cl(2)	89.3(2)
C(1)#3-Ru(1)-Cl(2)	89.3(2)
Cl(1)-Ru(1)-Cl(2)	180.000(1)
C(1)-N(1)-C(2)	174.7(5)
N(1)-C(1)-Ru(1)	177.9(6)
C(7)-C(2)-C(3)	124.0(4)
C(7)-C(2)-N(1)	118.1(4)
C(3)-C(2)-N(1)	117.8(5)
C(2)-C(3)-C(4)	115.0(6)
C(2)-C(3)-C(9)	120.1(5)
C(4)-C(3)-C(9)	124.8(6)
C(5)-C(4)-C(3)	121.6(6)
C(6)-C(5)-C(4)	121.1(6)
C(5)-C(6)-C(7)	121.3(7)
C(6)-C(7)-C(2)	116.9(6)

C(6)-C(7)-C(8)	121.5(6)
C(2)-C(7)-C(8)	121.6(4)

Symmetry transformations used to generate equivalent atoms:
#1 -y+1,x+1,z #2 y-1,-x+1,z #3 -x,-y+2,z

Table S6a. Crystallographic Data for **$(1b{\cdot}Br_2)_n$.**

Compound	**$(1b{\cdot}Br_2)_n$**
Formula	$C_{36}H_{36}Br_2Cl_2N_4Ru$
FW	856.48
Cryst syst	Triclinic
Space group	*P-1*
a (Å)	9.5670(10)
b (Å)	10.4897(6)
c (Å)	10.6910(10)
α(°)	67.358(7)
β (°)	79.414(10)
γ(°)	75.292(7)
V (Å^3)	953.31(14)
F(000)	428
μ/mm^{-1}	2.676
Z, ρ_c (g.cm^{-3})	1, 1.492
2Θ range (°)	3.17 to 27.50
Cryst size (mm^3)	0.53 x 0.3 x 0.31
Reflns. collected	8174
Indep. Reflns./Rint	4347 /0.0178
Data/restraints/param	4347 / 0 / 205
R_1/wR_2 (I>2σ(I))[a]	0.1005/ 0.3330
R_1/wR_2(all data)[a]	0.1295/ 0.3693
$\Delta\rho_{max}/\Delta\rho_{min}$ (e·Å^{-3})	5.441/ -2.927
GOF (on F^2)[a]	1.543

Table S6b. Bond lengths [A] and angles [deg] for **$(1b{\cdot}Br_2)_n$.**

Ru(1)-C(11)	1.981(11)
Ru(1)-C(11)#1	1.981(11)
Ru(1)-C(1)	1.995(9)
Ru(1)-C(1)#1	1.995(9)
Ru(1)-Cl(1)#1	2.560(2)
Ru(1)-Cl(1)	2.560(2)
Br(1)-Br(1)#2	2.7297(18)

N(1)-C(1)	1.134(12)
N(1)-C(2)	1.405(12)
C(5)-C(6)	1.373(19)
C(5)-C(4)	1.408(16)
C(11)-N(2)	1.170(13)
C(3)-C(4)	1.384(14)
C(3)-C(2)	1.392(14)
C(3)-C(8)	1.489(17)
C(2)-C(7)	1.361(15)
C(12)-C(17)	1.356(17)
C(12)-C(13)	1.379(18)
C(12)-N(2)	1.393(14)
C(6)-C(7)	1.391(15)
C(9)-C(7)	1.496(17)
C(14)-C(15)	1.27(2)
C(14)-C(13)	1.379(17)
C(16)-C(15)	1.39(3)
C(16)-C(17)	1.49(2)
C(13)-C(18)	1.50(2)
C(17)-C(19)	1.44(2)

C(11)-Ru(1)-C(11)#1	180.000(1)
C(11)-Ru(1)-C(1)	91.5(4)
C(11)#1-Ru(1)-C(1)	88.5(4)
C(11)-Ru(1)-C(1)#1	88.5(4)
C(11)#1-Ru(1)-C(1)#1	91.5(4)
C(1)-Ru(1)-C(1)#1	180.0(6)
C(11)-Ru(1)-Cl(1)#1	91.6(3)
C(11)#1-Ru(1)-Cl(1)#1	88.4(3)
C(1)-Ru(1)-Cl(1)#1	85.3(3)
C(1)#1-Ru(1)-Cl(1)#1	94.7(3)
C(11)-Ru(1)-Cl(1)	88.4(3)
C(11)#1-Ru(1)-Cl(1)	91.6(3)
C(1)-Ru(1)-Cl(1)	94.7(3)
C(1)#1-Ru(1)-Cl(1)	85.3(3)
Cl(1)#1-Ru(1)-Cl(1)	180.00(9)
C(1)-N(1)-C(2)	171.9(11)
C(6)-C(5)-C(4)	122.1(11)
N(2)-C(11)-Ru(1)	176.5(9)
C(4)-C(3)-C(2)	119.3(10)
C(4)-C(3)-C(8)	120.3(10)
C(2)-C(3)-C(8)	120.4(9)
C(7)-C(2)-C(3)	122.7(9)
C(7)-C(2)-N(1)	120.3(10)
C(3)-C(2)-N(1)	116.9(9)
C(17)-C(12)-C(13)	123.5(12)

C(17)-C(12)-N(2)	118.4(12)
C(13)-C(12)-N(2)	118.0(10)
C(11)-N(2)-C(12)	171.4(11)
C(5)-C(6)-C(7)	119.5(11)
N(1)-C(1)-Ru(1)	176.9(9)
C(3)-C(4)-C(5)	117.7(11)
C(2)-C(7)-C(6)	118.6(11)
C(2)-C(7)-C(9)	120.2(11)
C(6)-C(7)-C(9)	121.2(12)
C(15)-C(14)-C(13)	122.1(16)
C(15)-C(16)-C(17)	116.6(13)
C(14)-C(13)-C(12)	118.0(13)
C(14)-C(13)-C(18)	123.2(14)
C(12)-C(13)-C(18)	118.8(12)
C(12)-C(17)-C(19)	121.2(14)
C(12)-C(17)-C(16)	115.7(14)
C(19)-C(17)-C(16)	122.9(13)
C(14)-C(15)-C(16)	123.8(16)

Symmetry transformations used to generate equivalent atoms:
#1 -x+1,-y+1,-z #2 -x+1,-y,-z+1

Table S7. Bond lengths [Å] and angles [deg] for **$(1b{\cdot}I_2)_n$**

C(8)-C(3)	1.510(10)
C(9)-C(7)	1.506(8)
C(11)-N(2)	1.164(8)
C(11)-Ru(1)	1.978(6)
C(12)-C(17)	1.377(10)
C(12)-N(2)	1.393(8)
C(12)-C(13)	1.428(10)
C(13)-C(14)	1.371(10)
C(13)-C(18)	1.482(12)
C(14)-C(15)	1.309(14)
C(15)-C(16)	1.334(15)
C(16)-C(17)	1.472(14)
C(17)-C(19)	1.494(14)
C(1)-N(1)	1.154(7)
C(1)-Ru(1)	1.987(6)
C(2)-C(7)	1.382(8)
C(2)-C(3)	1.388(8)
C(2)-N(1)	1.399(7)
C(3)-C(4)	1.376(9)
C(4)-C(5)	1.371(10)
C(5)-C(6)	1.378(9)
C(6)-C(7)	1.384(8)
Cl(1)-Ru(1)	2.5048(14)
I(1)-I(1)#1	2.7376(10)
Ru(1)-C(11)#2	1.978(6)
Ru(1)-C(1)#2	1.987(6)
Ru(1)-Cl(1)#2	2.5048(14)
N(2)-C(11)-Ru(1)	177.0(5)
C(17)-C(12)-N(2)	120.3(7)
C(17)-C(12)-C(13)	122.0(7)
N(2)-C(12)-C(13)	117.8(6)
C(14)-C(13)-C(12)	118.1(8)
C(14)-C(13)-C(18)	121.1(8)
C(12)-C(13)-C(18)	120.7(6)
C(15)-C(14)-C(13)	120.8(10)
C(14)-C(15)-C(16)	124.3(10)
C(15)-C(16)-C(17)	119.5(8)
C(12)-C(17)-C(16)	115.3(8)
C(12)-C(17)-C(19)	118.9(8)
C(16)-C(17)-C(19)	125.8(8)
C(11)-N(2)-C(12)	171.3(6)
N(1)-C(1)-Ru(1)	175.6(5)
C(7)-C(2)-C(3)	123.5(5)

C(7)-C(2)-N(1)	117.3(5)
C(3)-C(2)-N(1)	119.2(5)
C(4)-C(3)-C(2)	117.5(6)
C(4)-C(3)-C(8)	121.6(6)
C(2)-C(3)-C(8)	120.9(6)
C(5)-C(4)-C(3)	120.3(6)
C(4)-C(5)-C(6)	121.3(6)
C(5)-C(6)-C(7)	120.3(6)
C(2)-C(7)-C(6)	117.1(5)
C(2)-C(7)-C(9)	120.9(5)
C(6)-C(7)-C(9)	121.9(6)
C(1)-N(1)-C(2)	171.5(6)
C(11)-Ru(1)-C(11)#2	180.0
C(11)-Ru(1)-C(1)#2	90.6(2)
C(11)#2-Ru(1)-C(1)#2	89.4(2)
C(11)-Ru(1)-C(1)	89.4(2)
C(11)#2-Ru(1)-C(1)	90.6(2)
C(1)#2-Ru(1)-C(1)	180.0(4)
C(11)-Ru(1)-Cl(1)	88.31(17)
C(11)#2-Ru(1)-Cl(1)	91.69(17)
C(1)#2-Ru(1)-Cl(1)	93.68(17)
C(1)-Ru(1)-Cl(1)	86.32(17)
C(11)-Ru(1)-Cl(1)#2	91.69(17)
C(11)#2-Ru(1)-Cl(1)#2	88.31(17)
C(1)#2-Ru(1)-Cl(1)#2	86.32(17)
C(1)-Ru(1)-Cl(1)#2	93.68(17)
Cl(1)-Ru(1)-Cl(1)#2	180.00(6)

Symmetry transformations used to generate equivalent atoms:
#1 -x,-y+1,-z-1 #2 -x,-y,-z

Table S8. Bond lengths [Å] and angles [deg] for **$(1b{\cdot}2I_2)_n$**.

Ru(1)-C(1)#1	1.985(12)
Ru(1)-C(1)	1.985(12)
Ru(1)-C(2)	2.004(12)
Ru(1)-C(2)#1	2.004(12)
Ru(1)-Cl(1)#1	2.583(2)
Ru(1)-Cl(1)	2.583(2)
I(1)-I(3)	2.751(3)
C(1)-N(1)	1.149(16)
C(2)-N(21)	1.131(15)
C(11)-C(12)	1.39(2)

C(11)-C(16)	1.40(2)
C(11)-N(1)	1.410(16)
C(12)-C(13)	1.41(2)
C(12)-C(18)	1.46(2)
C(13)-C(14)	1.39(3)
C(14)-C(15)	1.29(3)
C(15)-C(16)	1.41(2)
C(16)-C(17)	1.48(2)
C(21)-C(22)	1.364(18)
C(21)-C(26)	1.384(19)
C(21)-N(21)	1.429(15)
C(22)-C(23)	1.385(18)
C(22)-C(27)	1.55(2)
C(23)-C(24)	1.32(2)
C(24)-C(25)	1.39(2)
C(25)-C(26)	1.394(19)
C(26)-C(28)	1.47(3)
C(1)#1-Ru(1)-C(1)	180.0(6)
C(1)#1-Ru(1)-C(2)	88.8(5)
C(1)-Ru(1)-C(2)	91.2(5)
C(1)#1-Ru(1)-C(2)#1	91.2(5)
C(1)-Ru(1)-C(2)#1	88.8(5)
C(2)-Ru(1)-C(2)#1	180.0(6)
C(1)#1-Ru(1)-Cl(1)#1	89.3(4)
C(1)-Ru(1)-Cl(1)#1	90.7(4)
C(2)-Ru(1)-Cl(1)#1	86.6(4)
C(2)#1-Ru(1)-Cl(1)#1	93.4(4)
C(1)#1-Ru(1)-Cl(1)	90.7(4)
C(1)-Ru(1)-Cl(1)	89.3(4)
C(2)-Ru(1)-Cl(1)	93.4(4)
C(2)#1-Ru(1)-Cl(1)	86.6(4)
Cl(1)#1-Ru(1)-Cl(1)	180.0
N(1)-C(1)-Ru(1)	178.4(11)
N(21)-C(2)-Ru(1)	173.2(11)
C(12)-C(11)-C(16)	123.6(12)
C(12)-C(11)-N(1)	119.4(12)
C(16)-C(11)-N(1)	117.0(11)
C(11)-C(12)-C(13)	118.2(16)
C(11)-C(12)-C(18)	120.1(13)
C(13)-C(12)-C(18)	121.7(16)
C(14)-C(13)-C(12)	116.5(17)
C(15)-C(14)-C(13)	124.5(16)
C(14)-C(15)-C(16)	121.8(17)
C(11)-C(16)-C(15)	114.6(14)
C(11)-C(16)-C(17)	121.4(13)
C(15)-C(16)-C(17)	124.0(15)

C(22)-C(21)-C(26)	124.7(11)
C(22)-C(21)-N(21)	116.6(11)
C(26)-C(21)-N(21)	118.7(11)
C(21)-C(22)-C(23)	116.4(12)
C(21)-C(22)-C(27)	121.6(12)
C(23)-C(22)-C(27)	122.0(12)
C(24)-C(23)-C(22)	121.9(12)
C(23)-C(24)-C(25)	121.3(12)
C(24)-C(25)-C(26)	119.9(13)
C(21)-C(26)-C(25)	115.8(12)
C(21)-C(26)-C(28)	121.7(13)
C(25)-C(26)-C(28)	122.5(14)
C(1)-N(1)-C(11)	169.1(13)
C(2)-N(21)-C(21)	173.9(13)

Symmetry transformations used to generate equivalent atoms: #1 -x+1,-y+1,-z

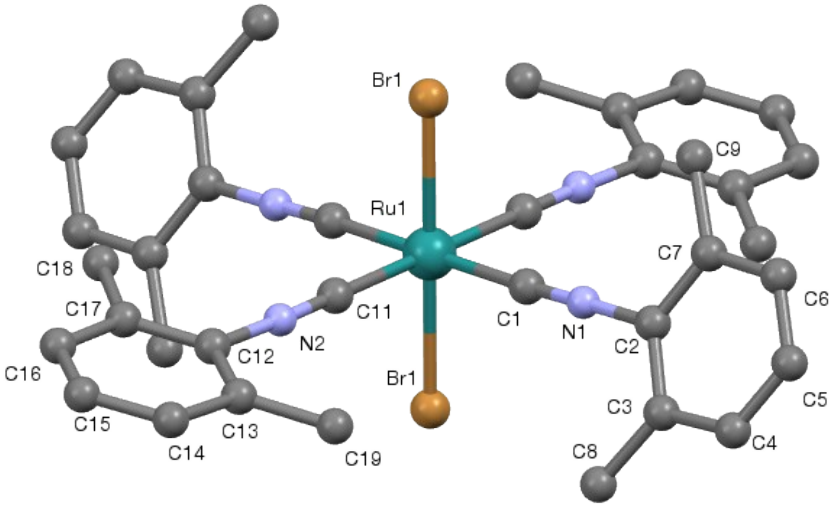

Figure S3. Molecular structure of **2b.**

Table S9. Bond lengths [Å] and angles [deg] for **2b.H_2O**

Ru(1)-C(1)#1	1.982(6)
Ru(1)-C(1)	1.982(6)
Ru(1)-C(11)#1	1.993(6)
Ru(1)-C(11)	1.993(6)
Ru(1)-Br(1)	2.5159(8)
Ru(1)-Br(1)#1	2.5159(8)
N(1)-C(1)	1.154(8)
N(1)-C(2)	1.393(8)

N(2)-C(11)	1.148(7)
N(2)-C(12)	1.403(7)
C(2)-C(3)	1.387(10)
C(2)-C(7)	1.393(9)
C(3)-C(4)	1.393(10)
C(3)-C(8)	1.507(11)
C(4)-C(5)	1.363(14)
C(5)-C(6)	1.368(15)
C(6)-C(7)	1.356(11)
C(7)-C(9)	1.500(13)
C(12)-C(13)	1.388(8)
C(12)-C(17)	1.394(8)
C(13)-C(14)	1.391(8)
C(13)-C(19)	1.491(9)
C(14)-C(15)	1.377(11)
C(15)-C(16)	1.367(11)
C(16)-C(17)	1.394(9)
C(17)-C(18)	1.494(9)

C(1)#1-Ru(1)-C(1)	180.00(14)
C(1)#1-Ru(1)-C(11)#1	90.4(2)
C(1)-Ru(1)-C(11)#1	89.6(2)
C(1)#1-Ru(1)-C(11)	89.6(2)
C(1)-Ru(1)-C(11)	90.4(2)
C(11)#1-Ru(1)-C(11)	180.000(1)
C(1)#1-Ru(1)-Br(1)	92.04(17)
C(1)-Ru(1)-Br(1)	87.96(17)
C(11)#1-Ru(1)-Br(1)	89.02(17)
C(11)-Ru(1)-Br(1)	90.98(17)
C(1)#1-Ru(1)-Br(1)#1	87.96(17)
C(1)-Ru(1)-Br(1)#1	92.04(17)
C(11)#1-Ru(1)-Br(1)#1	90.98(17)
C(11)-Ru(1)-Br(1)#1	89.02(17)
Br(1)-Ru(1)-Br(1)#1	180.000(1)
C(1)-N(1)-C(2)	178.2(6)
C(11)-N(2)-C(12)	178.0(6)
N(1)-C(1)-Ru(1)	177.3(6)
C(3)-C(2)-N(1)	117.7(6)
C(3)-C(2)-C(7)	124.3(6)
N(1)-C(2)-C(7)	118.0(6)
C(2)-C(3)-C(4)	115.4(7)
C(2)-C(3)-C(8)	120.6(6)
C(4)-C(3)-C(8)	124.0(7)
C(5)-C(4)-C(3)	121.1(8)
C(6)-C(5)-C(4)	121.1(7)
C(7)-C(6)-C(5)	121.0(8)

C(6)-C(7)-C(2)	117.0(8)
C(6)-C(7)-C(9)	121.4(8)
C(2)-C(7)-C(9)	121.6(7)
N(2)-C(11)-Ru(1)	179.2(5)
C(13)-C(12)-C(17)	124.4(5)
C(13)-C(12)-N(2)	117.9(5)
C(17)-C(12)-N(2)	117.7(5)
C(12)-C(13)-C(14)	116.5(6)
C(12)-C(13)-C(19)	122.4(5)
C(14)-C(13)-C(19)	121.1(6)
C(15)-C(14)-C(13)	120.6(6)
C(16)-C(15)-C(14)	121.4(6)
C(15)-C(16)-C(17)	120.8(6)
C(12)-C(17)-C(16)	116.3(6)
C(12)-C(17)-C(18)	121.2(6)
C(16)-C(17)-C(18)	122.5(6)

Symmetry transformations used to generate equivalent atoms: #1 -x+1/2,-y+3/2,-z+1

Table S10. Bond lengths [Å] and angles [deg] for **(2b·Br_2)$_n$.**

Ru(1)-C(41)	1.987(9)
Ru(1)-C(31)	1.989(8)
Ru(1)-C(21)	1.995(9)
Ru(1)-C(11)	2.001(9)
Ru(1)-Br(1)	2.4923(16)
Ru(1)-Br(2)	2.4958(16)
Br(3)-Br(4)	2.3662(17)
N(1)-C(11)	1.142(11)
N(1)-C(12)	1.390(10)
N(2)-C(21)	1.156(11)
N(2)-C(22)	1.393(11)
N(3)-C(31)	1.155(11)
N(3)-C(32)	1.396(10)
N(4)-C(41)	1.163(11)
N(4)-C(42)	1.398(10)
C(12)-C(17)	1.384(12)
C(12)-C(13)	1.411(12)
C(13)-C(14)	1.392(13)
C(13)-C(19)	1.483(13)
C(14)-C(15)	1.369(14)

C(15)-C(16)	1.385(13)
C(16)-C(17)	1.384(12)
C(17)-C(18)	1.513(12)
C(22)-C(23)	1.383(16)
C(22)-C(27)	1.407(17)
C(23)-C(24)	1.398(18)
C(23)-C(29)	1.51(2)
C(24)-C(25)	1.35(3)
C(25)-C(26)	1.38(3)
C(26)-C(27)	1.36(2)
C(27)-C(28)	1.51(2)
C(32)-C(33)	1.395(12)
C(32)-C(37)	1.399(12)
C(33)-C(34)	1.377(12)
C(33)-C(39)	1.498(12)
C(34)-C(35)	1.403(14)
C(35)-C(36)	1.349(13)
C(36)-C(37)	1.403(12)
C(37)-C(38)	1.503(12)
C(42)-C(47)	1.391(13)
C(42)-C(43)	1.395(12)
C(43)-C(44)	1.384(13)
C(43)-C(49)	1.478(15)
C(44)-C(45)	1.353(16)
C(45)-C(46)	1.373(16)
C(46)-C(47)	1.396(14)
C(47)-C(48)	1.508(14)

C(41)-Ru(1)-C(31)	91.0(3)
C(41)-Ru(1)-C(21)	177.6(4)
C(31)-Ru(1)-C(21)	90.6(3)
C(41)-Ru(1)-C(11)	92.3(3)
C(31)-Ru(1)-C(11)	176.5(3)
C(21)-Ru(1)-C(11)	86.0(3)
C(41)-Ru(1)-Br(1)	88.4(3)
C(31)-Ru(1)-Br(1)	88.7(2)
C(21)-Ru(1)-Br(1)	93.4(3)
C(11)-Ru(1)-Br(1)	92.5(3)
C(41)-Ru(1)-Br(2)	89.8(3)
C(31)-Ru(1)-Br(2)	91.6(2)
C(21)-Ru(1)-Br(2)	88.4(3)
C(11)-Ru(1)-Br(2)	87.3(3)
Br(1)-Ru(1)-Br(2)	178.17(5)
C(11)-N(1)-C(12)	169.8(8)
C(21)-N(2)-C(22)	169.2(9)
C(31)-N(3)-C(32)	172.4(9)

C(41)-N(4)-C(42)	171.0(9)
N(1)-C(11)-Ru(1)	176.0(8)
C(17)-C(12)-N(1)	118.3(7)
C(17)-C(12)-C(13)	123.6(8)
N(1)-C(12)-C(13)	118.2(8)
C(14)-C(13)-C(12)	115.7(8)
C(14)-C(13)-C(19)	122.5(9)
C(12)-C(13)-C(19)	121.8(9)
C(15)-C(14)-C(13)	121.7(9)
C(14)-C(15)-C(16)	121.0(9)
C(15)-C(16)-C(17)	120.0(9)
C(12)-C(17)-C(16)	118.0(8)
C(12)-C(17)-C(18)	120.1(8)
C(16)-C(17)-C(18)	121.9(8)
N(2)-C(21)-Ru(1)	174.9(8)
C(23)-C(22)-N(2)	117.5(10)
C(23)-C(22)-C(27)	125.0(11)
N(2)-C(22)-C(27)	117.5(10)
C(22)-C(23)-C(24)	115.3(15)
C(22)-C(23)-C(29)	121.4(10)
C(24)-C(23)-C(29)	123.2(14)
C(25)-C(24)-C(23)	121.2(17)
C(24)-C(25)-C(26)	121.7(13)
C(27)-C(26)-C(25)	120.8(17)
C(26)-C(27)-C(22)	116.0(15)
C(26)-C(27)-C(28)	122.4(15)
C(22)-C(27)-C(28)	121.6(10)
N(3)-C(31)-Ru(1)	177.2(7)
C(33)-C(32)-N(3)	119.3(8)
C(33)-C(32)-C(37)	123.0(8)
N(3)-C(32)-C(37)	117.7(8)
C(34)-C(33)-C(32)	117.5(8)
C(34)-C(33)-C(39)	121.7(8)
C(32)-C(33)-C(39)	120.8(8)
C(33)-C(34)-C(35)	120.5(8)
C(36)-C(35)-C(34)	121.1(9)
C(35)-C(36)-C(37)	120.8(8)
C(32)-C(37)-C(36)	117.1(8)
C(32)-C(37)-C(38)	121.0(8)
C(36)-C(37)-C(38)	121.8(8)
N(4)-C(41)-Ru(1)	178.9(8)
C(47)-C(42)-C(43)	123.5(8)
C(47)-C(42)-N(4)	118.2(8)
C(43)-C(42)-N(4)	118.3(8)
C(44)-C(43)-C(42)	116.6(9)
C(44)-C(43)-C(49)	122.5(9)

C(42)-C(43)-C(49)	120.9(9)
C(45)-C(44)-C(43)	121.7(9)
C(44)-C(45)-C(46)	120.7(9)
C(45)-C(46)-C(47)	121.0(10)
C(42)-C(47)-C(46)	116.3(9)
C(42)-C(47)-C(48)	121.5(9)
C(46)-C(47)-C(48)	122.2(9)

Table S11. Bond lengths [Å] and angles [deg] for **$(2b \cdot I_2)_n$**

Ru(1)-C(21)#1	1.994(7)
Ru(1)-C(21)	1.994(7)
Ru(1)-C(11)#1	1.994(6)
Ru(1)-C(11)	1.994(6)
Ru(1)-Br(1)#1	2.5635(9)
Ru(1)-Br(1)	2.5635(9)
I(1)-I(1)#2	2.7437(12)
C(11)-N(1)	1.141(8)
C(12)-C(13)	1.386(9)
C(12)-C(17)	1.389(9)
C(12)-N(1)	1.403(7)
C(13)-C(14)	1.384(9)
C(13)-C(18)	1.503(10)
C(14)-C(15)	1.359(10)
C(15)-C(16)	1.373(10)
C(16)-C(17)	1.390(8)
C(17)-C(19)	1.506(9)
C(21)-N(2)	1.153(8)
C(22)-C(27)	1.359(10)
C(22)-N(2)	1.394(9)
C(22)-C(23)	1.403(10)
C(23)-C(24)	1.386(10)
C(23)-C(28)	1.483(11)
C(24)-C(25)	1.333(12)
C(25)-C(26)	1.346(13)
C(26)-C(27)	1.423(12)
C(27)-C(29)	1.505(12)

C(21)#1-Ru(1)-C(21)	180.000(1)
C(21)#1-Ru(1)-C(11)#1	91.5(2)
C(21)-Ru(1)-C(11)#1	88.5(2)
C(21)#1-Ru(1)-C(11)	88.5(2)
C(21)-Ru(1)-C(11)	91.5(2)
C(11)#1-Ru(1)-C(11)	180.000(1)
C(21)#1-Ru(1)-Br(1)#1	88.45(17)
C(21)-Ru(1)-Br(1)#1	91.55(17)
C(11)#1-Ru(1)-Br(1)#1	93.95(17)
C(11)-Ru(1)-Br(1)#1	86.05(17)
C(21)#1-Ru(1)-Br(1)	91.55(17)
C(21)-Ru(1)-Br(1)	88.45(17)
C(11)#1-Ru(1)-Br(1)	86.05(17)
C(11)-Ru(1)-Br(1)	93.95(17)
Br(1)#1-Ru(1)-Br(1)	180.0
N(1)-C(11)-Ru(1)	175.1(5)
C(13)-C(12)-C(17)	123.2(5)
C(13)-C(12)-N(1)	120.0(5)
C(17)-C(12)-N(1)	116.8(5)
C(14)-C(13)-C(12)	117.2(6)
C(14)-C(13)-C(18)	121.6(6)
C(12)-C(13)-C(18)	121.2(6)
C(15)-C(14)-C(13)	120.9(6)
C(14)-C(15)-C(16)	121.3(6)
C(15)-C(16)-C(17)	120.3(6)
C(12)-C(17)-C(16)	117.1(6)
C(12)-C(17)-C(19)	121.0(5)
C(16)-C(17)-C(19)	121.9(6)
N(2)-C(21)-Ru(1)	177.8(5)
C(27)-C(22)-N(2)	119.1(6)
C(27)-C(22)-C(23)	123.3(7)
N(2)-C(22)-C(23)	117.6(6)
C(24)-C(23)-C(22)	116.8(7)
C(24)-C(23)-C(28)	121.2(7)
C(22)-C(23)-C(28)	122.0(6)
C(25)-C(24)-C(23)	121.0(8)
C(24)-C(25)-C(26)	121.9(8)
C(25)-C(26)-C(27)	120.7(8)
C(22)-C(27)-C(26)	116.2(8)
C(22)-C(27)-C(29)	120.7(7)
C(26)-C(27)-C(29)	123.1(8)
C(11)-N(1)-C(12)	172.0(6)
C(21)-N(2)-C(22)	171.4(6)

Symmetry transformations used to generate equivalent atoms: #1 -x,-y+1,-z+1 #2 -x,-y,-z+2

Table S12. Bond lengths [Å] and angles [deg] for **$(3b \cdot I_2)_n$**

Ru(1)-C(2)	1.993(5)
Ru(1)-C(2)#1	1.993(5)
Ru(1)-C(1)#1	1.995(5)
Ru(1)-C(1)	1.995(5)
Ru(1)-I(1)	2.7104(4)
Ru(1)-I(1)#1	2.7104(4)
I(2)-I(2)#2	2.7695(7)
N(1)-C(1)	1.145(6)
N(1)-C(10)	1.409(6)
N(2)-C(2)	1.147(6)
N(2)-C(20)	1.400(6)
C(10)-C(11)	1.391(7)
C(10)-C(15)	1.390(7)
C(11)-C(12)	1.391(7)
C(11)-C(16)	1.503(8)
C(12)-C(13)	1.358(9)
C(13)-C(14)	1.387(9)
C(14)-C(15)	1.386(7)
C(15)-C(17)	1.489(8)
C(20)-C(21)	1.391(6)
C(20)-C(25)	1.400(6)
C(21)-C(22)	1.383(7)
C(21)-C(26)	1.504(7)
C(22)-C(23)	1.380(7)
C(23)-C(24)	1.372(7)
C(24)-C(25)	1.380(7)
C(25)-C(27)	1.506(7)

C(2)-Ru(1)-C(2)#1	180.000(1)
C(2)-Ru(1)-C(1)#1	88.63(18)
C(2)#1-Ru(1)-C(1)#1	91.37(18)
C(2)-Ru(1)-C(1)	91.37(18)
C(2)#1-Ru(1)-C(1)	88.63(18)
C(1)#1-Ru(1)-C(1)	180.000(1)
C(2)-Ru(1)-I(1)	94.47(14)
C(2)#1-Ru(1)-I(1)	85.53(14)
C(1)#1-Ru(1)-I(1)	90.79(13)
C(1)-Ru(1)-I(1)	89.21(13)
C(2)-Ru(1)-I(1)#1	85.53(14)
C(2)#1-Ru(1)-I(1)#1	94.47(14)
C(1)#1-Ru(1)-I(1)#1	89.21(13)
C(1)-Ru(1)-I(1)#1	90.79(13)
I(1)-Ru(1)-I(1)#1	180.0

C(1)-N(1)-C(10)	172.3(5)
C(2)-N(2)-C(20)	169.7(5)
N(1)-C(1)-Ru(1)	178.4(4)
N(2)-C(2)-Ru(1)	174.2(4)
C(11)-C(10)-C(15)	124.4(4)
C(11)-C(10)-N(1)	117.4(4)
C(15)-C(10)-N(1)	118.3(4)
C(10)-C(11)-C(12)	115.6(5)
C(10)-C(11)-C(16)	121.8(4)
C(12)-C(11)-C(16)	122.6(5)
C(13)-C(12)-C(11)	122.4(5)
C(12)-C(13)-C(14)	120.2(5)
C(13)-C(14)-C(15)	120.7(6)
C(14)-C(15)-C(10)	116.8(5)
C(14)-C(15)-C(17)	121.2(5)
C(10)-C(15)-C(17)	122.0(5)
C(21)-C(20)-N(2)	117.3(4)
C(21)-C(20)-C(25)	123.5(4)
N(2)-C(20)-C(25)	119.2(4)
C(22)-C(21)-C(20)	116.7(4)
C(22)-C(21)-C(26)	122.4(4)
C(20)-C(21)-C(26)	120.9(4)
C(23)-C(22)-C(21)	121.2(5)
C(24)-C(23)-C(22)	120.5(5)
C(23)-C(24)-C(25)	121.2(4)
C(24)-C(25)-C(20)	116.9(4)
C(24)-C(25)-C(27)	122.2(4)
C(20)-C(25)-C(27)	120.9(4)

Symmetry transformations used to generate equivalent atoms:
#1 -x,-y+1,-z+1 #2 -x,-y,-z+2