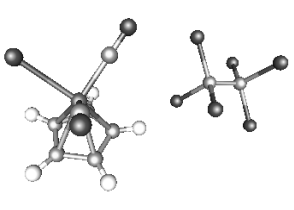
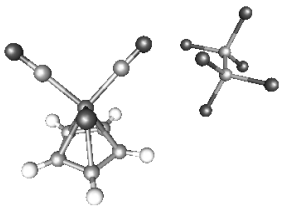
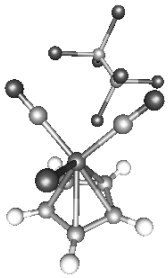
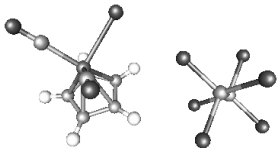
Electronic Supplementary Information: Supramolecular interactions between hexabromoethane and cyclopentadienyl ruthenium bromides: Halogen bonding or electrostatic organisation?

Rebecca O. Fuller, Christopher S. Griffith, George A. Koutsantonis,*, Kim M. Lapere, Brian W. Skelton, Mark A. Spackman, Allan H. White and Duncan A. Wild

Non-Covalent Interactions Between Hexabromoethane and Cyclopentadienyl Ruthenium Halides

A. Theoretical energy calculations and geometries from B3LYP 3-21G(all atoms)

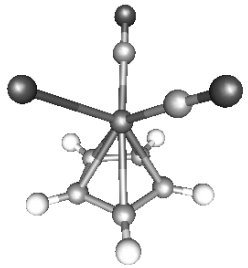
Schematic geometry and energetics from B3LYP 3-21G calculations

Isomer 1: Optimised from crystal structure as starting geometry	Isomer 2
	
E(start) = -22848.040224 E = -22848.126648 Minimum	E = -22848.125740 Minimum
Isomer 3	**Isomer 4**
	
E = -22848.126707 Transition State	E = -22848.131618 Minimum

B. Geometric parameters

All lengths are given in Å and angles in degrees.

1) Ru Complex, and C_2Br_6

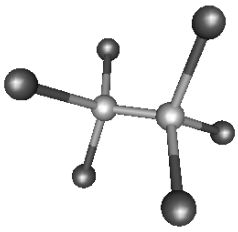


At the B3LYP (LANL2DZ for Ru & Br and I and 6-31G for C, H, F, O & Cl)

	F	Cl	Br	I		F	Cl	Br	I		F	Cl	Br	I
r(Ru-C)*	2.353	2.346	2.346	2.374	**r(C-H)**	1.079	1.079	1.080	1.079	∠	123.0	123.1	123.2	120.4
	2.335	2.319	2.320	2.324		1.080	1.080	1.080	1.080	**(Ru-C-H)**	122.1	122.0	122.0	122.0
η-C_5H_5	2.336	2.319	2.321	2.325		1.080	1.080	1.080	1.080		122.4	122.2	122.1	122.1
	2.364	2.355	2.356	2.358		1.079	1.079	1.079	1.079		122.7	122.8	122.8	122.7
	2.364	2.371	2.372	2.374		1.079	1.080	1.079	1.079		122.7	119.4	119.9	120.4
r(Ru-C(O))**	1.890	1.893	1.892	1.892	**r(C-O)**	1.171	1.170	1.171	1.171	∠	178.0	178.0	177.9	177.7
	1.890	1.894	1.893	1.892		1.172	1.170	1.171	1.171	**(Ru-C-O)**	176.7	177.2	177.1	176.9
r(Ru-X)	2.012	2.475	2.617	2.776										

* from front right, anti clockwise

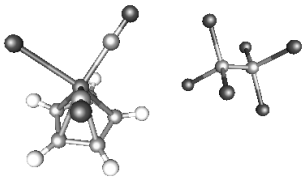
** front and then the one to the back



At the B3LYP level with LANL2DZ for Br and 6-31G for C

C_2H_6					
r(C-C)	1.548				
r(C-Br) †	2.040	∠ (Br-C-Br)	107.6	∠ (Br-C-C)	111.3

2) Crystal Start Isomer



RuComplex					
r(Ru-C)*	2.326	R(C-H)	1.080	∠ (Ru-C-H)	121.9
	2.317		1.079		122.5
η-C_5H_5	2.352		1.079		123.3
	2.374		1.079		120.0
	2.347		1.079		123.3
r(Ru-C(O))**	1.890	R(C-O)	1.171	∠ (Ru-C-O)	177.6
	1.894		1.170		177.9
r(Ru-Br)	2.620				
C_2H_6					
r(C-C)	1.547				
r(C-Br) †	2.035	∠ (Br-C-Br)	107.6		
front	2.045		107.6		
	2.045		107.6		
r(C-Br)‡	2.038		107.6		
back	2.042		107.6		
	2.039		107.9		
Intermolec					
r((C)O-Br)	4.224				
r(Ru-Br)	6.271				

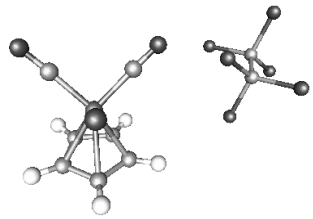
* from front right, anti clockwise

** front and then the one to the back right

† starting with the bromine closest to the CO of the Ru Complex, and moving clockwise

‡ starting with far right Bromine, and moving clockwise

3) Isomer 2



RuComplex					
r(Ru-C)*	2.383	R(C-H)	1.079	∠ (Ru-C-H)	119.8
	2.358		1.079		123.1
η-C_5H_5	2.323		1.080		122.4
	2.321		1.080		122.0
	2.351		1.079		122.9
r(Ru-C(O))**	1.890	R(C-O)	1.172	∠ (Ru-C-O)	177.7
	1.892		1.170		177.6
r(Ru-Br)	2.615				
C_2H_6					
r(C-C)	1.546				
r(C-Br) †	2.035	∠ (Br-C-Br)	107.9		
front	2.040		107.3		
	2.048		107.3		
r(C-Br)‡	2.040		107.6		
back	2.040		107.5		
	2.043		107.5		
Intermolec					
r((C)O-Br)	3.254				
r(Ru-Br)	5.578				

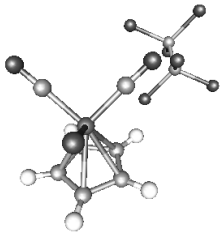
* from front right, anti clockwise

** right, then left

† starting with the bromine closest to the CO of the Ru Complex, and moving clockwise

‡ starting with top right bromine, and moving clockwise

4) Isomer 3



RuComplex					
r(Ru-C)*	2.381	R(C-H)	1.080	∠ (Ru-C-H)	120.5
	2.344		1.079		123.1
η-C_5H_5	2.322		1.080		121.0
	2.311		1.080		122.3
	2.367		1.079		123.3
r(Ru-C(O))**	1.885	R(C-O)	1.173	∠ (Ru-C-O)	176.6
	1.895		1.179		177.8
r(Ru-Br)	2.618				
C_2H_6					
r(C-C)	1.546				
r(C-Br) †	2.039	∠ (Br-C-Br)	107.8		
front	2.040		107.3		
	2.049		107.7		
r(C-Br)‡	2.039		107.8		
back	2.040		107.6		
	2.042		107.6		
Intermolec					
r((C)O-Br)	3.455				
r(Ru-Br)	5.170				

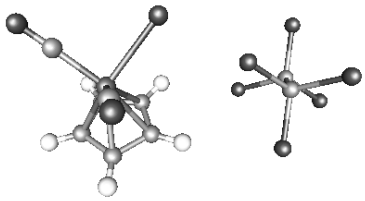
* from front right, anti clockwise

** right, then left

† starting with the bromine closest to the CO of the Ru Complex, and moving clockwise

‡ starting with top right bromine, and moving clockwise

5) Isomer 4



B3LYP LANL2DZ (RU,Br) 6-31G (C,H O)

RuComplex					
r(Ru-C)*	2.317	R(C-H)	1.080	∠ (Ru-C-H)	121.7
	2.346		1.079		123.1
η-C_5H_5	2.380		1.079		120.4
	2.356		1.079		123.6
	2.307		1.080		122.7
r(Ru-C(O))**	1.893	R(C-O)	1.170	∠ (Ru-C-O)	177.6
	1.896		1.170		177.5
r(Ru-Br)	2.630				
C_2H_6					
r(C-C)	1.542				
r(C-Br) †	2.053	∠ (Br-C-Br)	108.0		
front	2.040		107.4		
	2.050		107.4		
r(C-Br) †	2.052		107.3		
back	2.040		107.8		
	2.042		106.9		
Intermolec					
r(Br-Br)	3.374				
r(Ru-Br)	4.625				

* starting from the front and moving anti clockwise

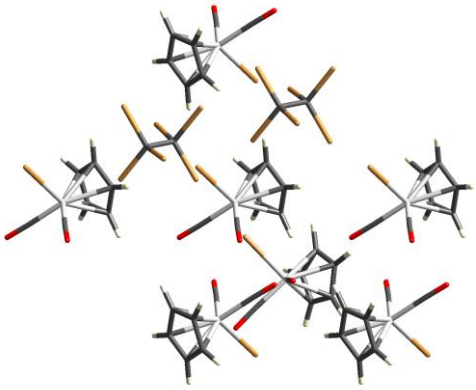
** front and then the one to the left

† starting with the bromine closest to the Ru Complex, and moving clockwise

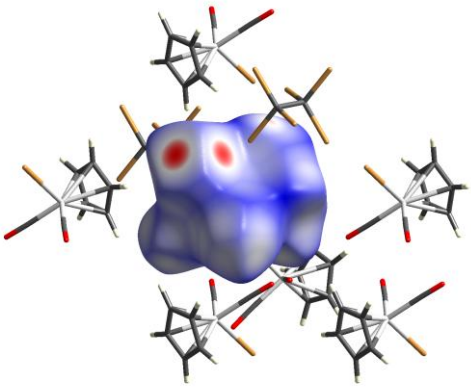
C. Interactions studies of polymorph monoclinic form

Fig S1 (a) Ru-Br-$(CO)_2$-η-C_5H_5 surrounded by its nearest neighbours. (b) A Hirshfeld surface mapped onto the central Ru-Br-$(CO)_2$-η-C_5H_5 the red focii around the Br atom indicate distances with contacts are less than the van der Waal radii. (c) A Hirshfeld surface was also mapped onto hexabromoethane. Rotation 180 ^{o} around *b* (c) shows additional short contacts on the Ru-Br-$(CO)_2$-η-C_5H_5 Hirshfeld surface.

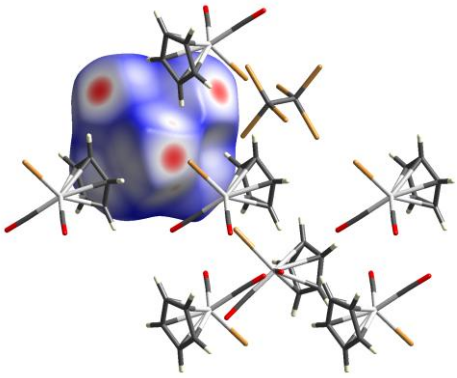
a



b



c



d

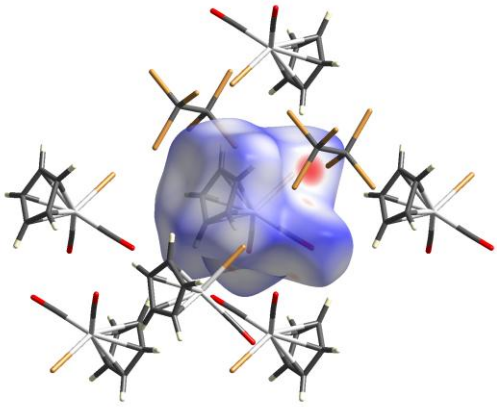
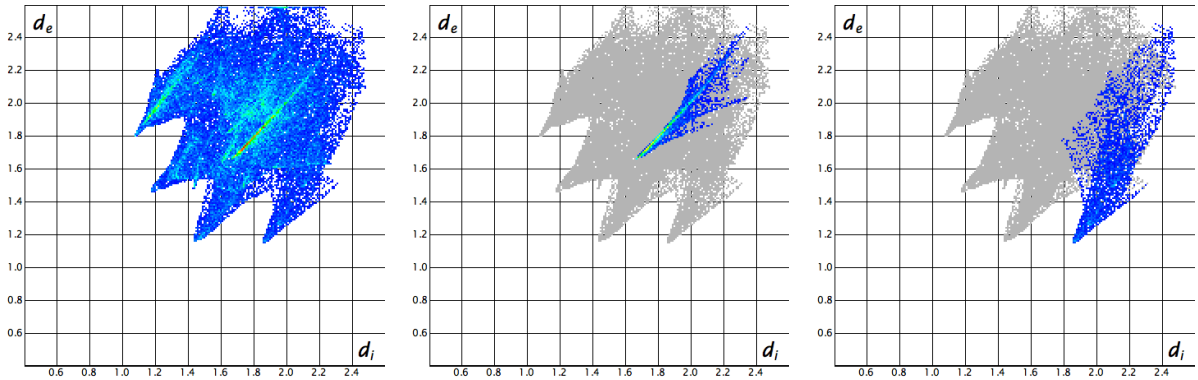


Fig S2 Fingerprint plot of (a) full Hirshfeld surface in Fig S1b. (b) Br...Br interactions make up 7.1 % and (c) Br...H interactions make up 8.0 % of the total plot.



a b c

Fig S3 Complimentary electrostatic potentials have been mapped onto molecules of (a) Ru-Br-$(CO)_2$-η-C_5H_5 and (b) hexabromoethane contained in the asymmetric unit cell of monoclinic form. For Ru-Br-$(CO)_2$-η-C_5H_5 the cell is rotated about b by 180^o. A strong negative potential is associated with the Br atom on the Ru-Br-$(CO)_2$-η-C_5H_5 molecule. Areas of positive potential are associated with the Br atoms contained in hexabromoethane.