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Electronic Supplementary Information (ESI)

Seemingly simple group 8 cyclopentadienyl metal halides: From little things, interesting things grow.†

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Table S1. Comparative geometries, $[CpM(CO)_2Cl]$ (M = Fe, Ru, Os)

Data for the Fe compound, ref.[10], other: this work

M	Fe (295 K)[10]	Ru (296 K)	Os
Distances (Å)			
M-C(Cp)	2.046(8)	2.191(3)	2.202(6)
	–2.097(7)	–2.258(3)	–2.299(6)
< >	2.06_9	2.22_3	2.24_7
M-C(0)(Cp)	1.71_2	1.87_2	1.88_8
M-C(CO)	1.774(5),	1.883(3),	1.884(6),
	1.767(6)	1.890(3)	1.896(6)
M-Cl	2.288(2)	2.4110(8)	2.4153(14)
Angles (degrees)			
C(0)-M-Cl	$122._8$	$123._3$	121.3_7
C(0)-M-C(CO)	$122._9$,	$124._6$,	124.0_1,
	$125._2$	$126._4$	127.3_9
C(CO)-M-C(CO)	94.0(3)	91.01(4)	90.4(3)
Cl-M-C(CO)	91.8(2),	90.81(11),	92.6(2),
	91.1(2)	90.24(9)	91.2(2)

*Values cited pertain to the major component of the chlorine atom and to the non-disordered carbonyl carbon. The $P2_1/n$ phase is common to both Ru and Os analogues; however, the determination of the Ru complex was executed at 296 K.

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Table S2. Comparative geometries, $[Cp^{(')}Ru(CO)_2X]$ (X = Cl, Br, I)*

(a) Cp complexes

X[Ref]	Cl	Br (296 K)[1]	Br·S (α)[16]	Br·S (β)(mol.1)[16]	(mol.2)[16]	I (173 K)[3,†]	Cl(Os)*
Distances (Å)							
Ru-C(Cp)	2.191(3)	2.16(2)	2.186(8)	2.208(6)	2.196(7)	2.213(8)	2.202(6)
	–2.258(3)	–2.26(3)	–2.240(5)	–2/263(7)	–2.260(7)	–2.271(3)	–2.299(6)
< >	2.22_3	2.22	2.21_4	2.23_5	2.22_9	2.24	2.24_7
Ru-C(0)(Cp)	1.87_2	1.87	1.87_0	1.88_0	1.87_9	1.88_8	1.88_8
Ru-C(CO)	1.883(3),	1.895(16),	1.884(8),	1.902(7),	1.887(7),	1.869(6),	1.884(6),
	1.890(3)	1.853(17)	1.922(7)	1.883(7)	1.891(8)	1.865(6)	1.896(6)
Ru-X	2.4110(8)	2.536(2)	2.5468(11)	2.5297(8)	2.5463(8)	2.7009(6)	2.4153(14)
Angles (degrees)							
C(0)-Ru-X	123.3_0	$123._3$	$121._7$	$123._2$	$122._7$	$120._5$	$121._4$
C(0)-Ru-C(CO)	$124._6$,	$125._3$,	$124._1$,	$126._0$,	$125._3$,	$126._3$,	$124._0$,
	$126._4$	$126._2$	$125._5$	$127._6$	$125._9$	$126._7$	$127._4$
C(CO)-Ru-C(CO)	91.01(14)	91.0(7)	93.7(3)	91.9(3)	92.3(3)	92.1(3)	90.4(3)
X-Ru-C(CO)	90.81(11),	90.8(5),	91.2(3),	88.1(2),	90.8(2),	90.9(2),	92.6(2),
	90.24(9)	89.7(5)	91.1(3)	87.8(2)	89.5(2)	89.9(2)	91.2(2)

*Data for the Os, Cl complex is also included. †Data for the major component (Cp disordered).

(b) Cp' complexes

X[Ref]	Cl	Br (298 K)[12]	Br*	I (298 K)[12]	I
Distances (Å)					
Ru-C(Cp')	2.191(2)	2.183(5)	2.201(2)	2.188(7)	2.189(4)
	–2.300(2)	–2.303(7)	–2.288(2)	–2.306(10)	–2.303(4)
< >	2.24	2.23	2.24	2.24	2.24
Ru-C(0)(Cp')	1.87_8	1.87_7	1.88_1	1.88_7	1.88_3
Ru-C(CO)	1.893(2),	1.885(6),	1.895(2),	1.874(8),	1.893(4),
	1.892(2)	1.881(6)	1.881(6)	1.882(9)	1.892(4)
Ru-X	2.4062(5)	2.535(2)	2.5005(6)	2.7030(4)	2.7104(6)
Angles (degrees)					
C(0)-Ru-X	$121._8$	$122._6$	$123._0$	$123._1$	$122._8$
C(0)-Ru-C(CO)	$125._6$,	$124._2$,	$125._3$,	$124._9$,	$124._3$
	$125._5$	$127._7$	$126._8$	$127._5$	$128._1$
C(CO)-Ru-C(CO)	91.77(8)	90.4(3)	91.1(2)	90.6(4)	90.7(2)
X-Ru-C(CO)	90.94(6),	92.6(2),	90.9(8),	91.6(3),	92.0(1),
	91.36(7)	88.8(2)	88.9(2)	88.2(3)	88.1(1)

*Values quoted for the present bromide are for the major component of disorder. The values for the iodide redetermination are harmonious with the previous,[12] but offer improved precision at lower temperature.

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Table S3. Coordination geometries, $[Cp^{x}Ru(CO)_2Cl]$

Data for $[Cp^*Ru(CO)_2Me]$ are included for comparison

Cp^x/X	Cp/Cl	Cp'/Cl	Cp*/Cl($P2_1/n$)	Cp*/Cl($P\bar{1}$)	Cp*/Me
Distances (Å)					
Ru-C(Cp)	2.191(3)	2.191(2)	2.200(1)	2.212(2)	2.253(1)
	–2.258(3)	–2.300(2)	–2.247(1)	–2.264(2)	–2.280(1)
< >	2.22_3	2.23_7	2.23_4	2.24_1	2.26_7
Ru-C(0)(Cp)	1.87_2	1.87_8	1.86_8	1.87_7	1.90_9
Ru-C(CO)	1.883(7),	1.893(2),	1.887(2),	1.852(4),	1.877(1),
	1.890(3)	1.892(2)	1.891(2)	–1.866(9)	1.880(1)
Ru-X	2.4110(8)	2.4062(5)	2.4315(4)	2.4407(11)	2.144(2)
Angles (degrees)					
C(0)-Ru-X	$123._3$	$121._8$	$120._1$	$120._6$	$121._0$
C(0)-Ru-C(CO)	$124._6$,	$125._6$,	$124._7$,	$124._5$,	$128._2$,
	$126._4$	$125._5$	$124._4$	$126._4$	$127._7$
C(CO)-Ru-C(CO)	91.01(14)	91.77(8)	92.52(7)	90.73(10)	90.32(5)
X-Ru-C(CO)	90.81(11),	90.94(6),	92.34(5),	93.08(5),	87.92(6),
	90.24(9)	91.36(7)	94.24(5)	92.28(12)	89.76(6)

*Major component

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Table S4. Coordination geometries, $[Cp^{Ph}Ru(CO)_2X]$ (X = Cl, I)

Values for the Cp counterparts are included for comparison, also that for $[Cp^{Ph}Ru(CO)_2H](\cdot\frac{1}{2}CH_2Cl_2)$

Cp^x/X	Cp/Cl	$Cp^{Ph}/Cl(\cdot\frac{1}{2}CH_2Cl_2)$ (mols. 1,2)	Cp/I	Cp^{Ph}/I[14]	Cp^{Ph}/H[14]
Distances (Å)					
Ru-C(Cp)	2.191(3)	2.211(3); 2.212(3)	2.213(8)	2.234(3)	2.251(3)
	–2.258(3)	–2.310(3; –2.321(3)	–2.271(3)	–2.317(3)	–2.286(3)
< >	2.22_3	2.26; 2.25	2.24	2.26_5	2.27
Ru-C(0)(Cp)	1.87_2	1.90_0, 1.89_1	1.88_3	1.90_2	1.91_1
Ru-C(CO)	1.883(7),	1.881(5), 1.879(5))	1.869(6),	1.866(4),	1.795(5)
	1.890(3)	1.912(4); 1.889(5)	1.865(6)	1.879(4)	1.811(5)
Ru-X	2.4110(8)	2.4118(11); 2.3967(10)	2.7009(6)	2.7230(4)	1.55(3)
Angles (degrees)					
C(0)-Ru-X	$123._3$	$124._7$, $123._1$	$120._5$	$128._0$	125
C(0)-Ru-C(CO)	$124._6$	$127._3$, $127._4$	$126._3$	$126._8$	$133._4$
	$126._4$	$128._7$, $128._0$	$126._7$	$127._6$	$130._9$
C(CO)-Ru-(CO)	91.01(14)	87.10(6); 89.0(2)	92.1(3)	90.61(18)	89.3(2)
X-Ru-C(CO)	90.81(11)	88.74(12); 89.51(13)	90.9(2),	84.23(12)	74.9(10)
	90.24(9)	87.16(14); 87.60(16)	89.9(2)	85.55(13)	82.8(10)

Table S5 Theoretical Geometric Parameters for the $Ru(MeCp)(CO)_2X$ complexes, where X = Cl, Br, and I calculated at the MP2 level of theory with 6-311G basis sets for C, H, O, Cl, and Br, and the LANLDZ basis set and ECP for Ru and I. Provided are bond lengths in Ångström and bond angles in degrees.

	r(Ru-X)	r(Ru-CO)	r(Ru-Cp)	∠(X-Ru-CO)	∠(CO-Ru-CO)	∠(X-Ru-Cp)	r(C-H)Cp	R(C-C)	R(C-H)Me
Chloro	2.474	1.866	1.927	90.0	90.9	119.4	1.082 1.081	1.496	1.097 1.093
Bromo	2.549	1.862	1.930	89.7	90.9	119.7	1.082 1.081	1.497	1.097 1.093
Iodo	2.719	1.858	1.938	89.7	90.9	119.9	1.082 1.081	1.498	1.098 1.093

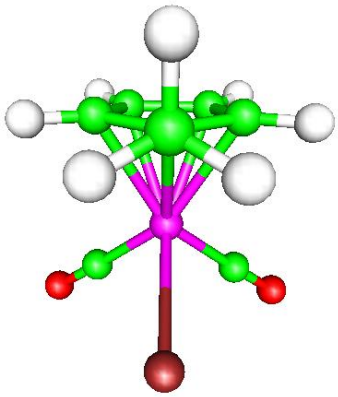

Figure S1. The optimised geometries of the one of the complexes is shown above.

Tables S6-S8: Calculated Atomic charges for the Chloro, Bromo, and Iodo complex, at the MP2 level of theory. Charges on hydrogens have been summed onto the associated Carbon atom. Also provided are the sums of the C and O charges for the carbonyls ligands.

[Note: The numbering of the carbons starts with the C attached to the methyl, and then goes clockwise looking down from the top C10 is the methyl carbon]

Table S5: Chloro data

	Mulliken	**NBO**	**Hirshfeld**
C1	3.16E-4	0.06704	0.00805
C2	-0.01402	0.01172	0.01242
C3	-0.01507	0.02448	0.0146
C4	-0.01506	0.0245	0.01461
C5	-0.0141	0.02448	0.01236
H6	0.0	0.0	0.0
H7	0.0	0.0	0.0
H8	0.0	0.0	0.0
H9	0.0	0.0	0.0
C10	0.07197	0.05185	0.06609
H11	0.0	0.0	0.0
H12	0.0	0.0	0.0
H13	0.0	0.0	0.0
Ru14	0.46512	-0.07675	0.15135
Cl15	-0.49928	-0.47787	-0.47642

C16	0.17756	0.40526	0.22661
O17	-0.1675	-0.22356	-0.12831
CO Sum	0.01006	0.1817	0.0983
C18	0.17756	0.40527	0.2266
O19	-0.1675	-0.22356	-0.12831
CO Sum	0.01006	0.18171	0.09829

Table S6: Bromo data

	Mulliken	**NBO**	**Hirshfeld**
C1	-9.31E-4	0.06662	0.00346
C2	-0.01707	0.01032	0.00797
C3	-0.01349	0.02842	0.01486
C4	-0.01341	0.02853	0.01495
C5	-0.01714	0.01017	0.0079
H6	0.0	0.0	0
H7	0.0	0.0	0
H8	0.0	0.0	0
H9	0.0	0.0	0
C10	0.06673	0.04757	0.06177
H11	0.0	0.0	0
H12	0.0	0.0	0
H13	0.0	0.0	0
Ru14	0.32627	-0.20946	0.10779
Br15	-0.3293	-0.33116	-0.37894
C16	0.17399	0.40512	0.21658
O17	-0.17481	-0.23062	-0.13649
CO Sum	-8.2E-4	0.1745	0.08009
C18	0.17398	0.40511	0.21657
O19	-0.17481	-0.23062	-0.13649
CO Sum	-8.3E-4	0.17449	0.08008

Table S7: Iodo Data

	Mulliken	**NBO**	**Hirshfeld**
C1	-0.136451	0.03151	0.03441
C2	0.126526	0.00766	0.01956
C3	-0.052017	0.05636	0.0429
C4	-0.052045	0.05640	0.04291
C5	0.126479	0.00760	0.01947
H6	-0.010958	-0.85450	-0.01754
H7	0.0	0.0	0
H8	0.0	0.0	0
H9	0.0	0.0	0
C10	0.059514	0.08465	0.07486
H11	0.0	0.0	0.0
H12	0.0	0.0	0
H13	0.0	0.0	0
Ru14	0.0	0.0	0
I15	-0.120405	-0.19879	-0.36923

C16	0.427693	0.94037	0.25552
O17	-0.398022	-0.53581	-0.17888
CO Sum	0.029671	0.40456	0.07664
C18	0.427700	0.94037	0.25553
O19	-0.398014	-0.53581	-0.17888
CO Sum	0.029686	0.40456	0.07665

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