Journal Name

ARTICLE TYPE

Cite this: DOI: 00.0000/xxxxxxxxxx

Supplementary Information

Unraveling the Enigma of Craig-Type Möbius-Aromatic Osmium Compounds

Antonia Rabe, Qian Wang and Dage Sundholm

Received Date
Accepted Date

DOI: 00.0000/xxxxxxxxxx

S1 Bond lengths

Table S1 Bond lengths (in pm) of **1**-**4** are calculated at the density functional theory (DFT) level using the ωB97X-D functional[S 1], def2-TZVP[S 2] basis sets and an effective core potential (ECP) on Os[S 3,S 4] to consider relativistic effects. The bond lengths are compared to experimental values.[S 5,S 6,S 7]

Molecule	**1**	**2**	**3**	**4**
Bond	bond length (exp.[S 5])	bond length (exp.[S 5])	bond length (exp.[S 6])	bond length (exp.[S 7])
Os - C1	199.94 (200.2)	182.23 (186.5)	206.22 (201.5)	203.73 (203.4)
C1 - C2	136.75 (137.2)	139.19 (137.3)	137.34 (140.1)	137.61 (134.4)
C2 - C3	142.19 (140.8)	142.17 (139.4)	143.36 (142.7)	145.32 (145.4)
C3 - C4	136.70 (137.7)	138.23 (140.2)	136.32 (134.9)	135.33 (134.7)
C4 - C5	141.65 (138.6)	139.86 (138.6)	143.57 (142.1)	145.23 (144.2)
C4 - Os	213.21 (214.9)	209.56 (208.7)	209.21 (208.9)	208.08 (210.2)
C5 - C6	138.21 (138.9)	138.73 (141.0)	137.19 (138.2)	134.98 (134.6)
C6 - C7	138.37 (138.7)	140.12 (139.3)	141.24 (143.9)	142.79 (142.2)
C7 - Os	194.76 (194.3)	206.99 (211.3)	180.03 (177.7)	206.95 (208.4)
C7 - C8	-	-	-	128.33 (130.7)
C8 - Os	-	-	-	223.26 (232.3)

S2 NMR chemical shift values

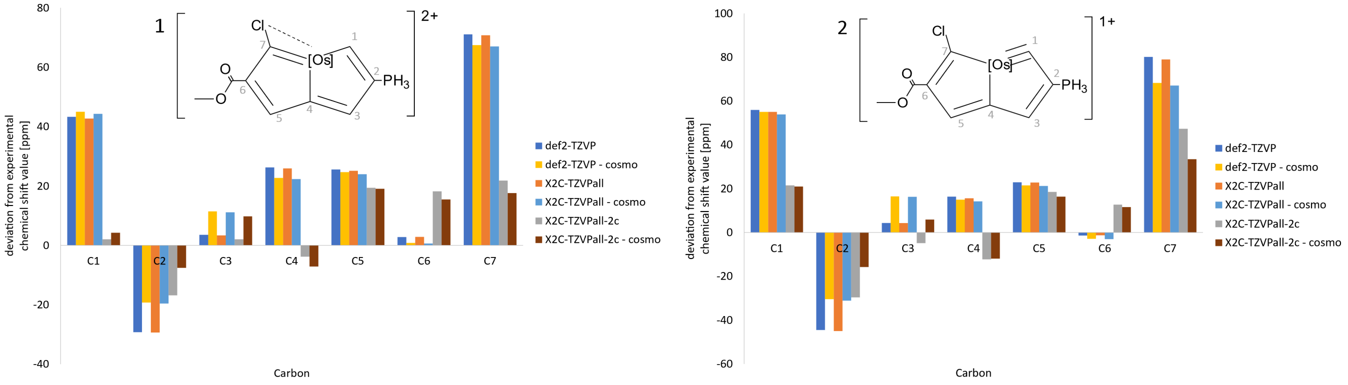


Fig. S1 The deviations of the ^{13}C NMR chemical shift values of **1** and **2** calculated at different levels of theory from experimental values.

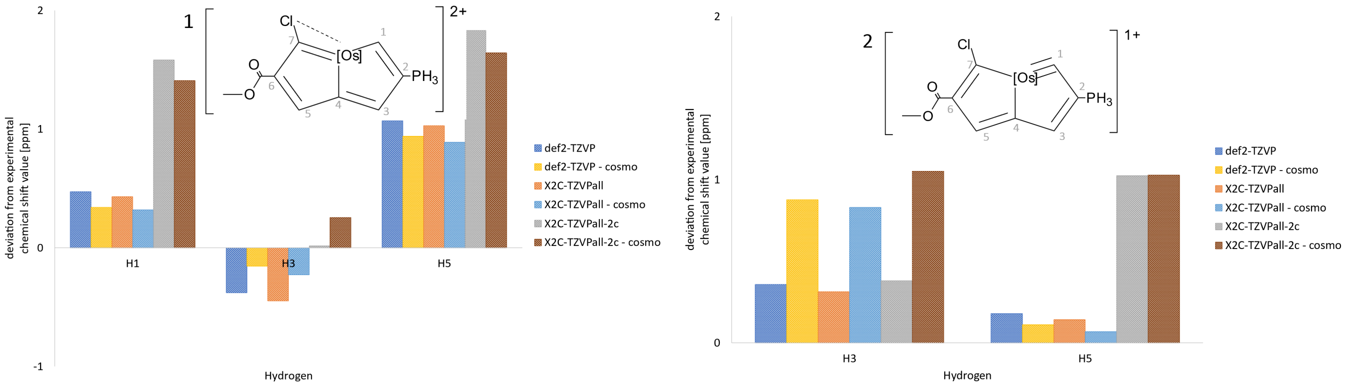


Fig. S2 The deviations of the ^{1}H NMR chemical shift values of **1** and **2** calculated at different levels of theory from experimental data.

Table S2 ^{13}C NMR chemical shift values (in ppm) of **1** calculated at the DFT level using the ωB97X-D functional[S1,S8] and different Hamiltonians[S9,S10,S4] and basis sets[S2,S11]. The experimental values are taken from Ref. S5.

1	ECP def2-TZVP	ECP def2-QZVP	X2C dyall-vdz(Os)/ x2c-SVPall	X2C x2c-SVPall	X2C x2c-TZVPall	SO-X2C x2c-SVPall-2c	SO-X2C x2c-TZVPall-2c	Exp.
C1	269.73	273.84	262.72	253.42	268.98	195.40	228.50	226.4
C2	109.48	111.05	105.23	102.28	109.25	119.24	121.90	138.7
C3	166.38	168.93	161.65	158.18	166.03	155.12	164.85	162.8
C4	214.95	217.50	205.76	202.53	214.47	163.34	184.90	188.7
C5	190.77	193.57	189.31	181.93	190.18	169.07	184.60	165.2
C6	152.93	155.46	148.41	146.00	152.81	167.54	168.33	150.1
C7	297.47	301.59	293.67	281.83	297.04	208.26	248.23	224.6
COOCH$_3$	162.16	165.36	153.24	153.29	162.18	150.80	160.49	157.7
COO**C**H$_3$	60.03	60.87	56.65	56.44	59.94	56.52	59.93	52.8

Table S3 ^{1}H NMR chemical shift values (in ppm) of **1** calculated at the DFT level using the ωB97X-D functional[S1,S8] and different Hamiltonians[S9,S10,S4] and basis sets[S2,S11]. The experimental values are taken from Ref. S5.

1	ECP def2-TZVP	ECP def2-QZVP	X2C dyall-vdz(Os)/ x2c-SVPall	X2C x2c-SVPall	X2C x2c-TZVPall	SO-X2C x2c-SVPall-2c	SO-X2C x2c-TZVPall-2c	Exp.
H1	14.07	14.21	14.05	13.70	14.03	14.85	15.18	13.60
H3	9.16	9.18	8.76	8.62	9.09	9.12	9.56	9.54
H5	10.01	10.03	9.85	9.63	9.97	10.56	10.77	8.94

Table S4 ^{13}C NMR chemical shift values (in ppm) of **2** calculated at the DFT level using the ωB97X-D functional[S1,S8] and different Hamiltonians[S9,S10,S4] and basis sets[S2,S11]. The experimental values are taken from Ref. S5.

2	ECP def2-TZVP	ECP def2-QZVP	X2C dyall-vdz(Os)/ x2c-SVPall	X2C x2c-SVPall	X2C x2c-TZVPall	SO-X2C x2c-SVPall-2c	SO-X2C x2c-TZVPall-2c	Exp.
C1	381.27	386.17	380.91	361.47	380.27	282.05	346.85	325.3
C2	82.09	83.19	81.53	76.44	81.46	97.60	97.01	126.6
C3	161.70	164.44	154.13	153.40	161.45	137.64	152.45	157.3
C4	197.15	199.57	192.14	184.17	196.27	147.49	168.53	180.8
C5	178.34	181.02	173.52	169.86	178.10	161.02	173.91	155.4
C6	155.04	157.70	149.55	147.80	155.00	167.07	169.12	156.4
C7	307.48	311.38	310.59	292.28	306.20	248.11	274.67	227.3
COOCH$_3$	166.25	169.18	157.00	157.01	166.26	155.57	165.48	163.1
COO**C**H$_3$	55.59	56.44	52.44	52.32	55.49	52.38	55.45	51.9

Table S5 ^{1}H NMR chemical shift values (in ppm) of **2** calculated at the DFT level using the ωB97X-D functional[S1,S8] and different Hamiltonians[S9,S10,S4] and basis sets[S2,S11]. The experimental values are taken from Ref. S5.

2	ECP def2-TZVP	ECP def2-QZVP	X2C dyall-vdz(Os)/ x2c-SVPall	X2C x2c-SVPall	X2C x2c-TZVPall	SO-X2C x2c-SVPall-2c	SO-X2C x2c-TZVPall-2c	Exp.
H3	8.06	8.07	7.66	7.50	8.01	7.74	8.08	7.70
H5	9.62	9.64	9.29	9.19	9.58	10.14	10.46	9.44

Table S6 ^{13}C NMR chemical shift values (in ppm) of **3** calculated at the DFT level using the ωB97X-D functional[S1,S8] and different Hamiltonians[S9,S10,S4] and basis sets[S2,S11]. The experimental values are taken from Ref. S6.

3	ECP def2-TZVP	ECP def2-QZVP	X2C dyall-vdz(Os)/ x2c-SVPall	X2C x2c-SVPall	X2C x2c-TZVPall	SO-X2C x2c-SVPall-2c	SO-X2C x2c-TZVPall-2c	Exp.
C1	267.18	271.54	268.36	251.50	265.49	219.30	243.55	224.2
C2	100.36	102.02	95.89	93.67	100.15	112.07	114.88	118.8
C3	148.16	150.47	143.67	140.62	147.83	137.09	146.43	147.8
C4	206.75	209.24	198.86	192.95	206.12	153.69	177.45	180.3
C5	187.86	190.68	182.12	178.36	187.66	155.87	172.63	162.0
C6	157.62	159.88	152.60	148.93	157.25	171.23	172.94	152.8
C7	388.84	394.25	392.73	369.89	387.52	299.27	358.90	330.8
COOCH$_3$	164.49	167.50	155.36	155.24	164.48	150.69	161.62	159.9
COO**C**H$_3$	55.67	56.51	52.51	52.36	55.58	52.31	55.45	51.6

Table S7 ^{1}H NMR chemical shift values (in ppm) of **3** calculated at the DFT level using the ωB97X-D functional[S1,S8] and different Hamiltonians[S9,S10,S4] and basis sets[S2,S11]. The experimental values are taken from Ref. S6.

3	ECP def2-TZVP	ECP def2-QZVP	X2C dyall-vdz(Os)/ x2c-SVPall	X2C x2c-SVPall	X2C x2c-TZVPall	SO-X2C x2c-SVPall-2c	SO-X2C x2c-TZVPall-2c	Exp.
H1	12.64	12.69	13.26	12.32	12.55	15.19	15.49	13.30
H3	8.57	8.59	8.17	8.03	8.53	8.93	9.43	8.99
H5	9.31	9.32	9.18	8.88	9.28	9.63	9.88	8.09

Table S8 ^{13}C NMR chemical shift values (in ppm) of **4** calculated at the DFT level using the ωB97X-D functional[S1,S8] and different Hamiltonians[S9,S10,S4] and basis sets[S2,S11]. The experimental values are taken from Ref. S7.

4	ECP def2-TZVP	ECP def2-QZVP	X2C dyall-vdz(Os)/ x2c-SVPall	X2C x2c-SVPall	X2C x2c-TZVPall	SO-X2C x2c-SVPall-2c	SO-X2C x2c-TZVPall-2c	Exp.
C1	278.90	283.22	276.12	261.47	277.49	238.83	261.67	232.16
C2	90.37	92.05	88.54	83.20	89.96	90.13	96.27	116.15
C3	138.05	140.46	133.77	131.25	137.79	144.84	146.71	141.19
C4	212.40	214.97	203.53	197.74	212.09	158.42	184.97	183.39
C5	186.93	189.69	179.68	177.04	186.62	178.86	189.25	163.72
C6	125.15	127.43	119.39	117.68	124.80	124.49	129.17	123.78
C7	198.58	201.90	179.14	185.24	198.96	166.71	186.80	181.74
C8	43.32	44.06	43.19	43.39	42.74	19.25	24.70	121.52[a]

[a] Probably incorrect assignment of the ^{13}C NMR signal of the C8 atom. The authors of Ref. S7 reported two ^{13}C NMR chemical shift for C8 of the related compound with para-methyl triphenyl posphine attached to C8. One of them agrees well with our calculated value.

Table S9 ^{1}H NMR chemical shift values (in ppm) of **4** calculated at the DFT level using the ωB97X-D functional[S1,S8] and different Hamiltonians[S9,S10,S4] and basis sets[S2,S11]. The experimental values are taken from Ref. S7.

4	ECP def2-TZVP	ECP def2-QZVP	X2C dyall-vdz(Os)/ x2c-SVPall	X2C x2c-SVPall	X2C x2c-TZVPall	SO-X2C x2c-SVPall-2c	SO-X2C x2c-TZVPall-2c	Exp.
H1	12.10	12.09	12.45	11.89	12.07	13.26	13.53	12.12
H3	7.26	7.26	6.82	6.72	7.23	6.66	7.23	6.45
H5	8.72	8.73	8.35	8.23	8.68	8.53	8.96	6.35
H6	6.50	6.51	6.14	6.14	6.46	6.16	6.45	4.97

S3 Difference between calculated and measured NMR chemical shifts

Table S10 Difference between calculated and measured ^{13}C NMR chemical shifts for **1** calculated at different levels of theory with and without considering solvent effects using COSMO.[S 12,S 13]

Molecule **1**	ECP def2-TZVP	ECP def2-TZVP COSMO	X2C X2C-TZVPall	X2C X2C-TZVPall COSMO	SO-X2C X2C-TZVPall-2c	SO-X2C X2C-TZVPall-2c COSMO
C1	43.3	45.0	42.6	44.3	2.1	4.3
C2	-29.2	-19.3	-29.4	-19.6	-16.8	-7.6
C3	3.6	11.5	3.2	11.2	2.0	9.8
C4	26.2	22.8	25.8	22.3	-3.8	-7.1
C5	25.6	24.7	25.0	24.0	19.4	19.1
C6	2.8	0.8	2.7	0.6	18.2	15.5
C7	72.9	69.3	72.4	68.8	23.6	19.4
COOCH$_3$	4.5	8.7	4.5	8.7	2.8	7.2
COO**C**H$_3$	7.2	5.6	7.1	5.5	7.1	5.5

Table S11 Difference between calculated and measured ^{1}H NMR chemical shifts for **1** calculated at different levels of theory with and without considering solvent effects using COSMO.[S 12,S 13]

Molecule **1**	ECP def2-TZVP	ECP def2-TZVP COSMO	X2C X2C-TZVPall	X2C X2C-TZVPall COSMO	SO-X2C X2C-TZVPall-2c	SO-X2C X2C-TZVPall-2c COSMO
H1	0.47	0.34	0.43	0.32	1.58	1.41
H3	-0.38	-0.16	-0.45	-0.23	0.02	0.25
H5	1.07	0.94	1.03	0.89	1.83	1.64

Table S12 Difference between calculated and measured ^{13}C NMR chemical shifts for **2** calculated at different levels of theory with and without considering solvent effects using COSMO.[S 12,S 13]

Molecule **2**	ECP def2-TZVP	ECP def2-TZVP COSMO	X2C X2C-TZVPall	X2C X2C-TZVPall COSMO	SO-X2C X2C-TZVPall-2c	SO-X2C X2C-TZVPall-2c COSMO
C1	56.0	55.1	55.0	53.9	21.5	21.0
C2	-44.5	-30.4	-45.1	-31.1	-29.6	-15.8
C3	4.4	16.5	4.2	16.3	-4.8	5.9
C4	16.3	15.0	15.5	14.2	-12.3	-11.9
C5	22.9	21.5	22.7	21.2	18.5	16.4
C6	-1.4	-2.9	-1.4	-3.0	12.7	11.6
C7	80.2	68.3	78.9	67.1	47.4	33.5
COOCH$_3$	3.2	7.2	3.2	7.3	2.4	6.6
COO**C**H$_3$	3.7	3.7	3.6	3.6	3.5	3.6

Table S13 Difference between calculated and measured ^{1}H NMR chemical shifts for **2** calculated at different levels of theory with and without considering solvent effects using COSMO.[S 12,S 13]

Molecule **2**	ECP def2-TZVP	ECP def2-TZVP COSMO	X2C X2C-TZVPall	X2C X2C-TZVPall COSMO	SO-X2C X2C-TZVPall-2c	SO-X2C X2C-TZVPall-2c COSMO
H3	0.36	0.88	0.31	0.83	0.38	1.05
H5	0.18	0.11	0.14	0.07	1.02	1.03

Table S14 Difference between calculated and measured ^{13}C NMR chemical shifts for **3** calculated at different levels of theory with and without considering solvent effects using COSMO.[S 12,S 13]

Molecule **3**	ECP def2-TZVP	ECP def2-TZVP COSMO	X2C X2C-TZVPall	X2C X2C-TZVPall COSMO	SO-X2C X2C-TZVPall-2c	SO-X2C X2C-TZVPall-2c COSMO
C1	43.0	40.1	41.3	38.6	19.3	15.3
C2	-18.4	-5.7	-18.6	-6.0	-3.9	8.0
C3	0.4	9.1	0.0	8.8	-1.4	6.8
C4	26.5	20.7	26.0	20.0	-2.8	-8.7
C5	25.9	27.1	25.7	26.8	10.6	13.2
C6	4.8	0.9	4.4	0.4	20.1	16.0
C7	58.0	52.0	56.7	50.6	28.1	26.8
COOCH$_3$	4.6	9.2	4.6	9.2	1.7	6.6
COO**C**H$_3$	4.1	4.1	4.0	4.0	3.9	3.9

Table S15 Difference between calculated and measured ^{1}H NMR chemical shifts for **3** calculated at different levels of theory with and without considering solvent effects using COSMO.[S 12,S 13]

Molecule **3**	ECP def2-TZVP	ECP def2-TZVP COSMO	X2C X2C-TZVPall	X2C X2C-TZVPall COSMO	SO-X2C X2C-TZVPall-2c	SO-X2C X2C-TZVPall-2c COSMO
H1	-0.66	-0.63	-0.75	-0.72	2.19	2.19
H3	-0.42	-0.17	-0.46	-0.21	0.44	0.72
H5	1.22	1.30	1.19	1.26	1.79	1.88

Table S16 Difference between calculated and measured ^{13}C NMR chemical shifts for **4** calculated at different levels of theory with and without considering solvent effects using COSMO.[S 12,S 13]

Molecule **4**	ECP def2-TZVP	ECP def2-TZVP COSMO	X2C X2C-TZVPall	X2C X2C-TZVPall COSMO	SO-X2C X2C-TZVPall-2c	SO-X2C X2C-TZVPall-2c COSMO
C1	46.74	40.94	45.33	39.68	29.51	24.35
C2	-25.78	-16.35	-26.19	-16.85	-19.88	-11.17
C3	-3.14	1.09	-3.40	0.76	5.52	9.65
C4	29.01	26.47	28.70	26.26	1.58	-2.00
C5	23.21	23.30	22.90	22.92	25.53	25.44
C6	1.37	-0.45	1.02	-0.76	5.39	3.42
C7	16.84	11.76	17.22	12.17	5.06	-0.10

Table S17 Difference between calculated and measured ^{1}H NMR chemical shifts for **4** calculated at different levels of theory with and without considering solvent effects using COSMO.[S 12,S 13]

Molecule **4**	ECP def2-TZVP	ECP def2-TZVP COSMO	X2C X2C-TZVPall	X2C X2C-TZVPall COSMO	SO-X2C X2C-TZVPall-2c	SO-X2C X2C-TZVPall-2c COSMO
H1	-0.02	-0.40	-0.05	-0.41	1.41	0.99
H3	0.81	0.88	0.78	0.84	0.78	0.78
H5	2.37	2.29	2.33	2.24	2.61	2.51
H6	1.53	1.37	1.49	1.33	1.48	1.32

S4 Magnetic shielding constants of reference compounds.

Table S18 Isotropic shielding constants (in ppm) for TMS calculated at the DFT level using the ωB97X-D functional[S 1,S 8] and different Hamiltonians[S 9,S 10,S 4] and basis sets[S 2,S 11].

Nucleus	ECP def2-TZVP	ECP def2-QZVP	X2C dyall-vdz(Os)/ x2c-SVPall	X2C x2c-SVPall	X2C x2c-TZVPall	SO-X2C x2c-SVPall-2c	SO-X2C x2c-TZVPall-2c
C	188.7541	187.5214	196.3534	196.0561	188.6838	195.7325	189.7060
H	31.9268	31.6440	31.7884	31.7703	31.9252	31.7758	31.9274

Table S19 Isotropic shielding constants, chemical shift values and deviations from experimental values (in ppm) for benzene calculated at the DFT level using the ωB97X-D functional[S 1,S 8] and different Hamiltonians[S 9,S 10,S 4] and basis sets[S 2,S 11]. The experimental chemical shift values are 128.3600 ppm for carbon and 7.3390 ppm for hydrogen.[S 14]

Shielding	ECP def2-TZVP	ECP def2-QZVP	X2C dyall-vdz(Os)/ x2c-SVPall	X2C x2c-SVPall	X2C x2c-TZVPall	SO-X2C x2c-SVPall-2c	SO-X2C x2c-TZVPall-2c
C	53.7633	50.2096	69.2383	69.0361	53.6598	68.5996	54.6769
H	24.2268	23.9424	24.4577	24.4440	24.2199	24.4223	24.1947
Shift							
C	134.9908	137.3118	127.1151	127.0200	135.0240	127.1330	135.0290
H	7.7000	7.7016	7.3307	7.3263	7.7053	7.3536	7.7328
Deviation							
C	6.6308	8.9518	-1.2449	-1.3400	6.6640	-1.2270	6.6690
H	0.3610	0.3626	-0.0083	-0.0127	0.3663	0.0146	0.3938

S5 Population analysis

Table S20 Natural Population Analysis (NPA) for **1**.[S 15] The phosphine hydrogen atoms are omitted and complete shell numbers removed. The total charge of **1** is +2.

Molecule 1	charge	n(s)	n(p)	n(d)	n(f)	sum valence
Os	0.26	0.49	0.00	7.25	0.01	8
C1	-0.14	1.08	3.05	0.01	0.00	4
C2	-0.53	1.00	3.52	0.01	0.00	4
C3	-0.12	0.98	3.13	0.01	0.00	4
C4	-0.17	1.01	3.16	0.01	0.00	4
C5	-0.01	1.00	3.00	0.01	0.00	4
C6	-0.27	0.97	3.29	0.01	0.00	4
C7	0.01	1.08	2.89	0.01	0.00	4
H1	0.24	0.76	0.00	0.00	0.00	1
H3	0.25	0.75	0.00	0.00	0.00	1
H5	0.26	0.74	0.00	0.00	0.00	1
Cl	0.27	1.80	4.90	0.02	0.00	7
COOCH$_3$	0.76	0.77	2.46	0.01	0.00	4
C***O***OCH$_3$	-0.54	1.70	4.82	0.02	0.00	6
CO***O***CH$_3$	-0.46	1.60	4.84	0.01	0.00	6
COO***C***H$_3$	-0.27	1.12	3.14	0.01	0.00	4
P	0.85	1.24	2.87	0.04	0.00	5
[Os] Cl	-0.36	1.91	5.44	0.01	0.00	7
[Os] P	0.34	1.38	3.24	0.04	0.00	5
[Os] P	0.34	1.38	3.24	0.04	0.00	5

Table S21 Natural Population Analysis (NPA) for **2**.[S 15] The phosphine hydrogen atoms are omitted and complete shell numbers removed. The total charge of **2** is $+1$.

Molecule 2	charge	n(s)	n(p)	n(d)	n(f)	sum valence
Os	0.22	0.47	0.00	7.31	0.01	8
C1	0.03	1.30	2.66	0.01	0.00	4
C2	-0.71	1.02	3.67	0.01	0.00	4
C3	-0.11	0.99	3.12	0.01	0.00	4
C4	-0.22	1.01	3.21	0.01	0.00	4
C5	-0.04	0.99	3.05	0.01	0.00	4
C6	-0.30	0.96	3.33	0.01	0.00	4
C7	-0.07	1.16	2.91	0.01	0.00	4
H3	0.22	0.78	0.00	0.00	0.00	1
H5	0.24	0.76	0.00	0.00	0.00	1
Cl	0.13	1.80	5.05	0.02	0.00	7
COOCH$_3$	0.75	0.79	2.45	0.01	0.00	4
C***O***OCH$_3$	-0.55	1.70	4.83	0.02	0.00	6
CO***O***CH$_3$	-0.48	1.61	4.85	0.01	0.00	6
COO***C***H$_3$	-0.26	1.11	3.15	0.01	0.00	4
P	0.89	1.21	2.85	0.05	0.00	5
[Os] Cl	-0.48	1.92	5.55	0.01	0.00	7
[Os] P	0.38	1.37	3.21	0.04	0.00	5
[Os] P	0.38	1.37	3.20	0.04	0.00	5

Table S22 Natural Population Analysis (NPA) for **3**.[S 15] The phosphine hydrogen atoms are omitted and complete shell numbers removed. The total charge of **3** is $+1$.

Molecule 3	charge	n(s)	n(p)	n(d)	n(f)	sum valence
Os	0.20	0.47	0.00	7.32	0.01	8
C1	-0.28	1.14	3.13	0.01	0.00	4
C2	-0.55	1.00	3.53	0.01	0.00	4
C3	-0.21	0.97	3.23	0.01	0.00	4
C4	-0.17	1.01	3.15	0.01	0.00	4
C5	-0.07	1.00	3.06	0.01	0.00	4
C6	-0.33	0.98	3.34	0.01	0.00	4
C7	0.14	1.30	2.54	0.01	0.00	4
H1	0.21	0.79	0.00	0.00	0.00	1
H3	0.22	0.78	0.00	0.00	0.00	1
H5	0.24	0.76	0.00	0.00	0.00	1
COOCH$_3$	0.75	0.78	2.45	0.01	0.00	4
C***O***OCH$_3$	-0.55	1.70	4.83	0.02	0.00	6
CO***O***CH$_3$	-0.47	1.61	4.85	0.01	0.00	6
COO***C***H$_3$	-0.26	1.11	3.15	0.01	0.00	4
P	0.86	1.22	2.87	0.04	0.00	5
[Os] Cl	-0.49	1.92	5.57	0.01	0.00	7
[Os] P	0.39	1.37	3.20	0.04	0.00	5
[Os] P	0.39	1.37	3.20	0.04	0.00	5

Table S23 Natural Population Analysis (NPA) for **4**.[S 15] The phosphine hydrogen atoms are omitted and complete shell numbers removed. The total charge of **4** is +1.

Molecule 4	charge	n(s)	n(p)	n(d)	n(f)	sum valence
Os	0.04	0.44	0.01	7.51	0.00	8
C1	-0.20	1.11	3.08	0.01	0.00	4
C2	-0.60	1.00	3.58	0.01	0.00	4
C3	-0.25	0.97	3.28	0.00	0.00	4
C4	-0.16	1.01	3.15	0.01	0.00	4
C5	-0.12	0.99	3.12	0.01	0.00	4
C6	-0.31	0.98	3.32	0.01	0.00	4
C7	0.11	0.92	2.96	0.01	0.00	4
C8	-0.75	0.98	3.75	0.01	0.01	4
H1	0.20	0.79	0.00	0.00	0.00	1
H3	0.21	0.79	0.00	0.00	0.00	1
H5	0.22	0.78	0.00	0.00	0.00	1
H6	0.24	0.76	0.00	0.00	0.00	1
P (C2)	0.88	1.21	2.86	0.05	0.00	5
P (C8)	0.93	1.18	2.83	0.06	0.00	5
[Os] Cl	-0.58	1.92	5.65	0.01	0.00	7
[Os] P	0.39	1.37	3.20	0.04	0.00	5
[Os] P	0.39	1.37	3.19	0.04	0.00	5

Table S24 Natural Population Analysis (NPA)[S 15] results for the osmium atom in molecules **1**-**4**.

Molecule	charge	n(s)	n(p)	n(d)	n(f)	sum valence
1 - Os	0.26	0.49	0.00	7.25	0.01	8
2 - Os	0.22	0.47	0.00	7.31	0.01	8
3 - Os	0.20	0.47	0.00	7.32	0.01	8
4 - Os	0.04	0.44	0.01	7.51	0.00	8

S6 Paratropic current density

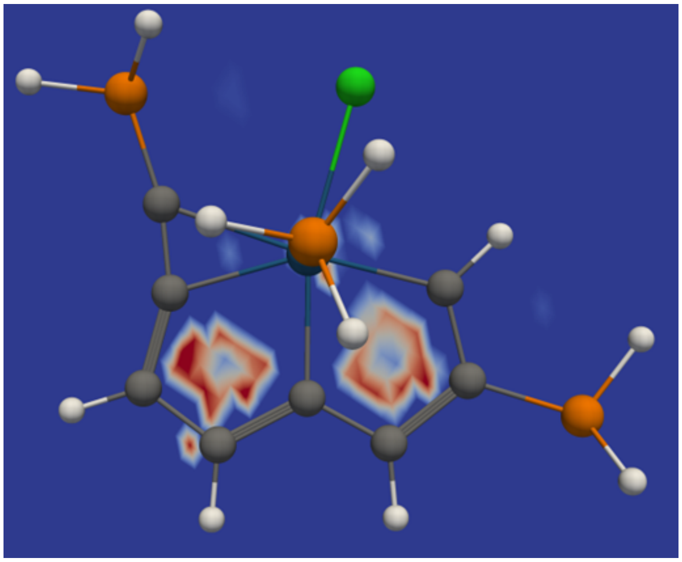


Fig. S3 The paratropic current-density pathways of **4**.

S7 Ring-current profiles

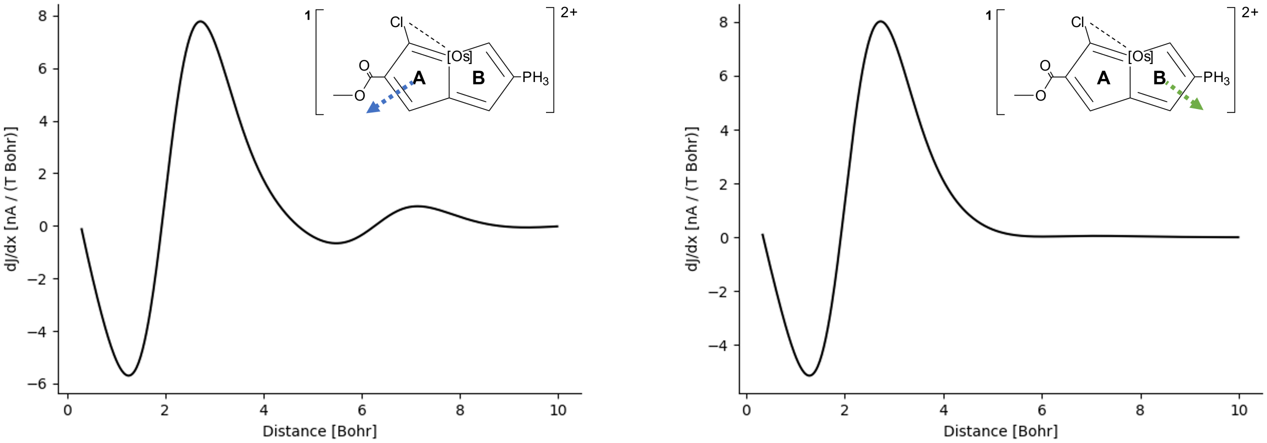


Fig. S4 The ring-current profile of **1** along the integration planes in ring A (left) and in ring B (right).

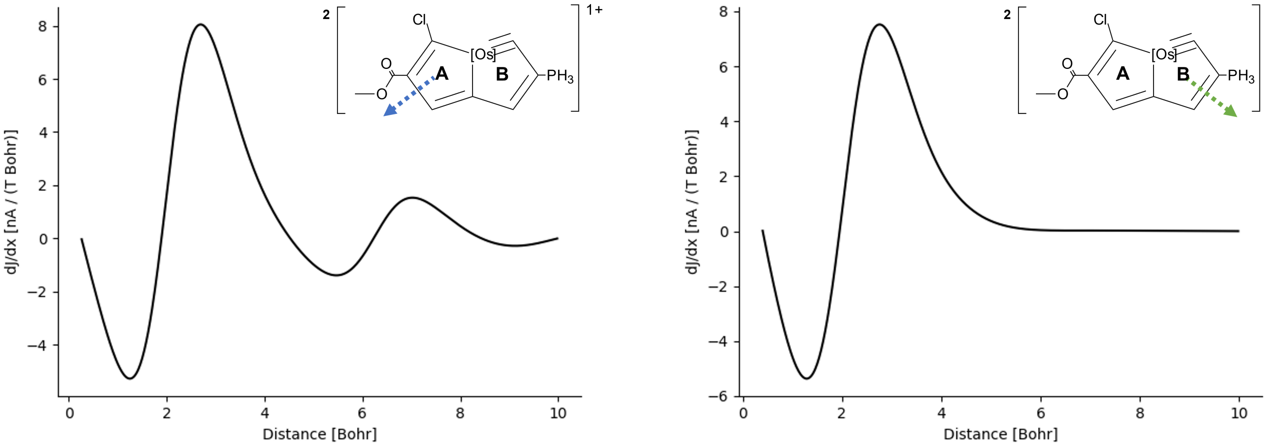


Fig. S5 The ring-current profile of **2** along the integration planes in ring A (left) and in ring B (right).

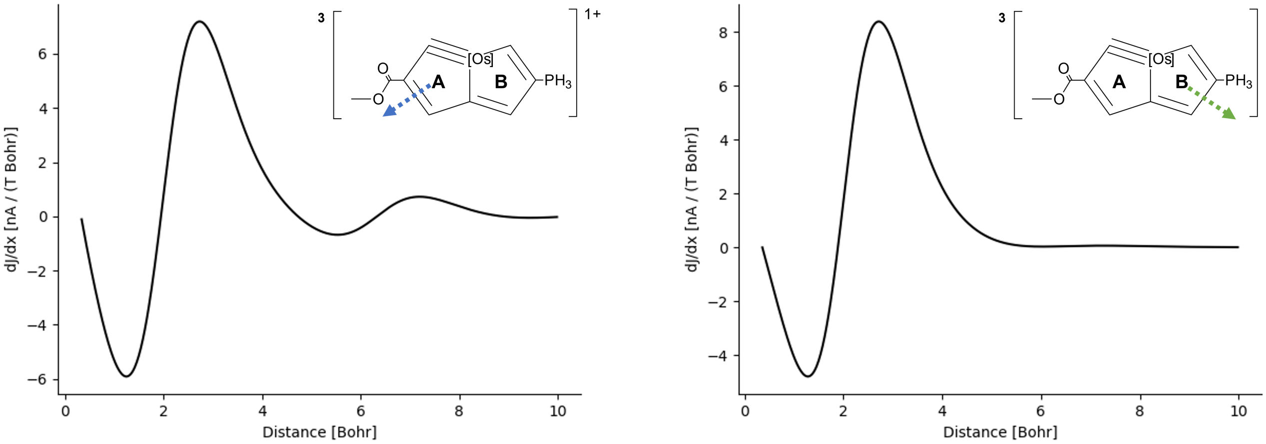


Fig. S6 The ring-current profile of **3** along the integration planes in ring A (left) and in ring B (right).

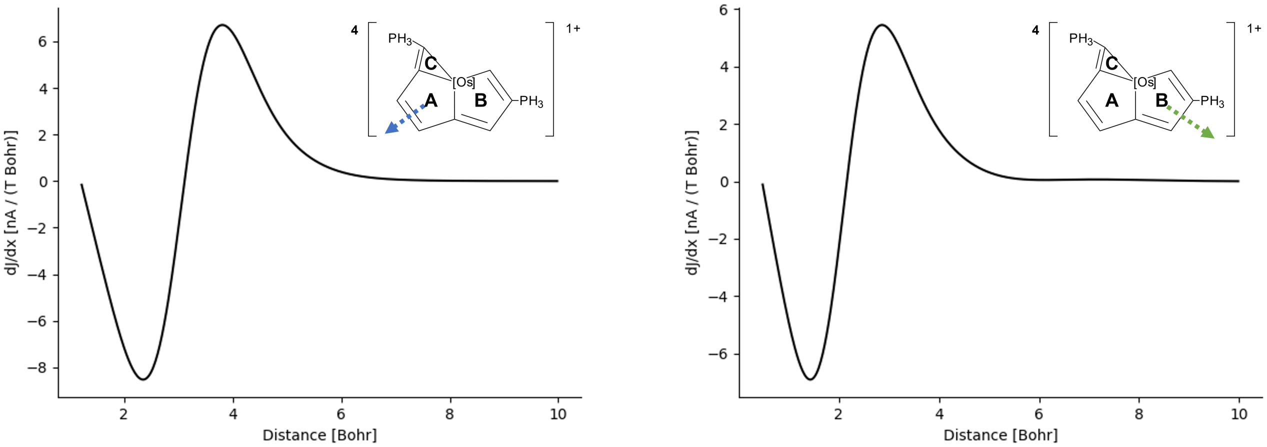


Fig. S7 The ring-current profile of **4** along the integration planes in ring A (left) and in ring B (right).

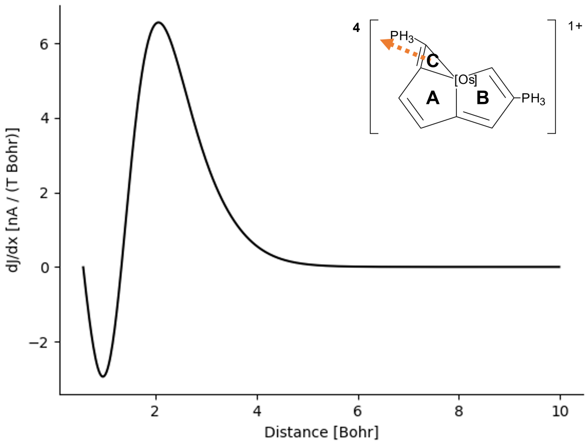
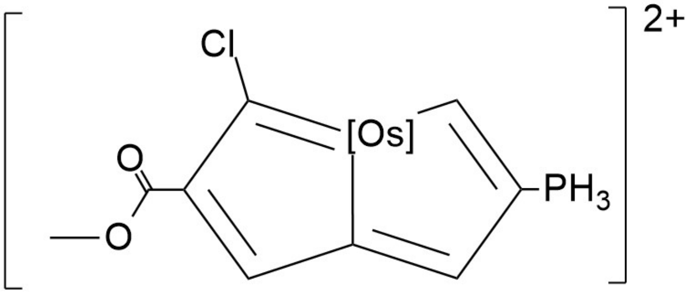


Fig. S8 The ring-current profile of 4 along the integration plane in ring C.

S8 Cartesian coordinates

All structures are optimised at DFT-level using the ωB97X-D functional[S 1] and the def2-TZVP basis sets[S 2]. Relativistic effects were considered by using an ECP[S 3,S 4] on Os.

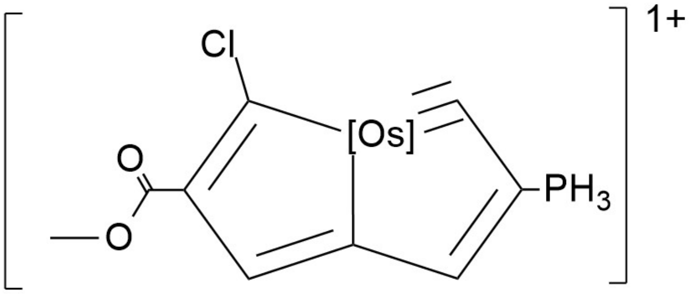
Molecule 1



Molecule 1, [Os] denotes $Os(PH_3)_2Cl$, Energy: -2537.1328 Hartree

32			
C	-0.941935	1.078695	0.000709
C	-1.589965	-0.143909	0.000436
C	-0.596194	-1.104499	0.001123
C	0.708048	-0.551811	0.000993
Os	0.943431	1.567232	-0.000007
C	2.781343	0.780132	-0.001374
C	3.020923	-0.566255	-0.000719
C	1.826530	-1.337783	0.000670
C	-3.082437	-0.305257	-0.000703
Cl	-1.582340	2.648784	0.001231
Cl	1.967502	3.692943	-0.001734
P	0.968937	1.827409	2.403190
O	-3.814037	0.643293	0.000856
O	-3.428193	-1.572753	-0.003761
C	-4.851534	-1.837118	-0.005347
H	-0.798739	-2.170362	0.001592
H	3.586635	1.510096	-0.002616
H	1.790732	-2.422282	0.001324
H	5.583986	-0.153279	0.002699
H	4.961303	-1.999878	-1.122318
H	0.789345	0.719980	3.245850
H	-0.021081	2.704368	2.872146
H	-4.944714	-2.916903	-0.009105
H	-5.302396	-1.402057	-0.893919
H	-5.303143	-1.408141	0.885811
H	2.132084	2.413810	2.917293
H	4.958962	-2.008179	1.113082
P	4.672208	-1.211954	-0.001956
P	0.965066	1.827343	-2.403295
H	-0.022821	2.708134	-2.869547
H	0.779305	0.720815	-3.245800
H	2.129127	2.409507	-2.920093

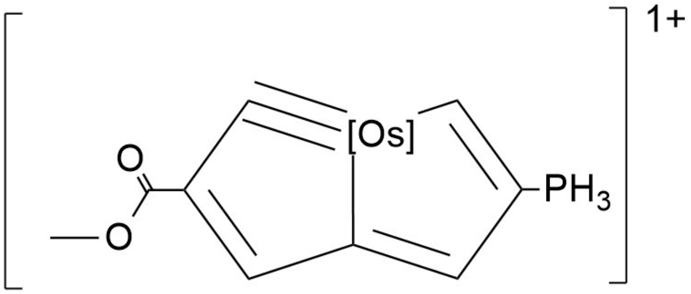
Molecule 2



Molecule 2, [Os] denotes $Os(PH_3)_2Cl$, Energy: -2536.8465 Hartree

31			
C	-1.576969	-0.908943	-0.109669
C	-1.323369	0.464605	0.002174
C	0.035266	0.730171	0.092236
C	0.867972	-0.391608	0.025954
Os	-0.024836	-2.276963	-0.173347
C	1.777208	-2.545339	-0.137835
C	2.811642	-1.621897	-0.016627
C	2.247463	-0.320416	0.079120
C	-2.356245	1.548901	-0.011501
Cl	-1.318787	-4.318382	-0.404366
P	-0.212570	-2.328536	-2.544878
O	-3.422288	1.467871	-0.550715
O	-1.919284	2.631362	0.633438
C	-2.827483	3.740376	0.651703
H	0.410360	1.742475	0.199765
H	2.815945	0.600169	0.178396
H	4.499132	-3.534033	-0.118208
H	5.195305	-1.832223	1.153068
H	0.382329	-1.351211	-3.361489
H	-1.530918	-2.298994	-3.019375
H	-2.324467	4.523965	1.208799
H	-3.756307	3.455353	1.141752
H	-3.044769	4.065832	-0.363704
H	0.260816	-3.502388	-3.144697
H	5.270745	-1.651303	-1.041904
P	4.467540	-2.143083	-0.003760
P	-0.366237	-2.752779	2.131188
H	0.175153	-1.948752	3.149281
H	-1.713407	-2.790898	2.516333
H	0.062243	-4.022814	2.537597
Cl	-3.189775	-1.457995	-0.160675

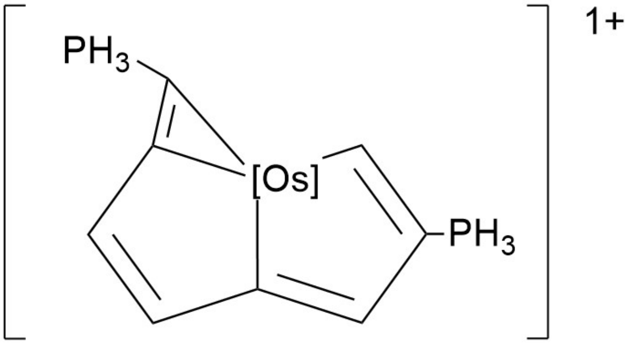
Molecule 3



Molecule 3, [Os] denotes Os$(PH_3)_2$Cl, Energy: -2077.2392 Hartree

31			
C	-1.220914	-2.850751	0.001770
H	-1.691775	-3.834237	0.002610
C	-1.994093	-1.715609	0.001047
C	-1.274904	-0.475433	0.000268
H	-1.752039	0.499921	-0.000268
C	0.076013	-0.657724	0.000452
C	1.041876	0.404545	0.000079
H	0.793466	1.461717	0.000089
C	2.326540	-0.076894	-0.000105
C	2.233476	-1.486206	-0.000089
C	3.620793	0.654749	0.000086
C	4.660675	2.743287	0.001337
H	4.348130	3.782133	0.000973
H	5.249913	2.516447	-0.884932
H	5.247845	2.516433	0.888974
H	0.014483	-3.838689	2.902292
H	2.150230	-3.554189	2.761284
H	0.862232	-1.885964	3.259230
H	0.826225	-1.898079	-3.261240
H	2.154119	-3.534775	-2.765467
H	0.024250	-3.867511	-2.887644
H	-4.129835	-3.179424	0.001341
H	-4.390728	-1.257933	-1.100137
H	-4.390934	-1.257532	1.101920
Cl	1.155806	-5.023769	0.002626
P	0.952832	-2.955072	2.351575
P	0.946932	-2.960469	-2.349062
P	-3.745865	-1.837314	0.001093
O	4.680768	0.093980	0.000435
O	3.451306	1.972556	0.000074
Os	0.827176	-2.610283	0.001077

Molecule 4



Molecule 4, [Os] denotes $Os(PH_3)_2Cl$, Energy: -2230.6164 Hartree

30			
Os	-1.677714	-1.929191	-0.000090
Cl	-2.439245	-4.312428	-0.000169
P	-1.698156	-1.999065	2.351669
P	-5.136707	-2.405696	-0.001931
P	-1.697118	-1.999320	-2.351748
P	2.918871	-2.168435	-0.000595
C	-3.030553	-0.363056	-0.000781
C	-1.246335	1.086151	-0.000073
H	-0.723744	2.038318	0.000082
C	0.241397	-2.612987	0.000143
H	0.484499	-3.676167	0.000020
C	-0.543467	-0.184733	-0.000071
C	-2.593117	0.996149	-0.000401
H	-3.278275	1.833172	-0.000545
C	0.805323	-0.295661	-0.000093
H	1.485579	0.551699	-0.000028
C	-3.836899	-1.361410	-0.001200
C	1.251645	-1.678655	-0.000157
H	-1.606660	-3.262014	-2.961442
H	-2.830120	-1.499825	-3.025880
H	-0.701459	-1.317945	-3.076154
H	3.691900	-1.746655	-1.094089
H	3.014218	-3.560784	0.002813
H	3.693456	-1.740760	1.089470
H	-0.702263	-1.318506	3.076550
H	-2.830900	-1.498849	3.025690
H	-1.608693	-3.261950	2.961057
H	-6.389603	-1.774955	-0.009080
H	-5.165631	-3.276102	-1.097833
H	-5.174994	-3.267248	1.100755

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