Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Supplementary Information

A Benchmark for Non-covalent Interactions in Organometallic Crystals

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Table S1. Choice of CCDC entry and calculated lattice energies for selected compounds.

Entry	CCDC ID	Calculated lattice energy [kJ/mol]		
		PBE-D3(BJ)/def2TZVP	**PBE-D3(BJ)/def2TZVPP**	**M06L/def2TZVPP**
08	CDCPTI03	120.94	120.17	108.25
	CDCPTI04	120.89	120.04	108.12
09	CEHPIO	95.26	94.85	83.00
	CEHPIO01	95.30	94.89	83.20
	CEHPIO02	95.65	95.23	85.33
13	**CUQUIN05**	177.11	175.01	158.13
	CUQUIN13	179.28	177.42	150.63
	CUQUIN18	180.30	178.04	153.78
31	QQQBWP02	132.81	131.63	132.55
	QQQBWP03	132.82	131.62	132.58
32	**TCBMNI**	178.90	177.90	155.77
	TCBMNI01	178.58	177.52	156.05
	TCBMNI02	178.56	177.50	155.97

Table S2. Difference in absolute energies for single crystal structures obtained at different temperatures for entry **02** Cr(II)$(acac)_2$.

	CCDC	T_{xtal}/K	Space group	Unit cell vectors/ Å a, b, c	Angles between unit cell vectors/°	Year
	ACACCS	295	P 2_1/n	11.445, 4.748, 10.325	*α* 90 *β* 91.60 *γ* 90	1977, ref. [1]
E/h	**PBE-D3(BJ)/def2-TZVP**					**-3468.666408**
	PBE-D3(BJ)/def2-TZVPP					**-3468.681996**
	M06-L/def2-TZVPP					**-3470.479550**
	ACACCS01	120	P 2_1/n	10.248, 4.701, 11.350	*α* 90 *β* 92.16 *γ* 90	2020, ref. [2]
E/h	**PBE-D3(BJ)/def2-TZVP**					**-3468.667136**
	PBE-D3(BJ)/def2-TZVPP					**-3468.682685**
	M06-L/def2-TZVPP					**-3470.480680**
ΔE/kJ mol^{-1}	**PBE-D3(BJ)/def2-TZVP**					**-1.9**
	PBE-D3(BJ)/def2-TZVPP					**-1.8**
	M06-L/def2-TZVPP					**-3.0**

Table S3. Experimental heats of sublimations; reported experimental errors and thermodynamic corrections for entries of the XTMC43 set.

Entry	**ΔH_{subl} [kJ/mol]**	**T_m [K][a]**	**Type of exp.**[b]	**Exp. error [kJ/mol][c]**	**$\Delta\bar{H}_{subl}$ [kJ/mol][d]**	**Largest exp. error [kJ/mol]**	**$-E_{latt,exp}$ [kJ/mol]**
01	126.8	298	ME	4.2	123.2 ± 7.8	4.2	128.2
	132.1		C	1.9			
	110.9		HSA	0.8			
	123.0		ME	3.0			
02	129.8	298	ME	8.7		8.7	134.8
03	122.5	298	-	1.2	120.8 ± 6.5	3.4	125.8
	127.1		-	1.2			
	127.0		-	1.1			

	116.6		C	2.0			
	115.1		-	2.1			
	127.5		-	3.2			
	109.9		C	3.4			
04	124.7	298	ME	3.8	122.4 ± 2.4	10.0	127.3
	120.0		E	10.0			
05	140.4	298	C	1.1		1.1	145.4
06	91.2	298	C	4.2	94.6 ± 3.4	4.2	99.5
	97.9		TE				
07	93.0	298	C	2.0	93.8 ± 0.8	4.2	98.8
	94.6		-	4.2			
08	124.4	298	ME	2.9	121.6 ± 2.8	2.9	126.6
	118.8		-	2.1			
09	104.6	298	-	8.4		8.4	109.6
10	134.6	298	ME	4.0		4.0	139.6
11	58.6	298	-	4.2		4.2	63.6
12	159.3	298	-	1.7	159.5 ± 0.3	4.0	164.5
	159.3		-	1.9			
	160.0		C	4.0			
13	168.7	298	ME	7.3	169.4 ± 0.7	7.3	174.3
	170.0		-	3.0			
14	78.2	298	-	6.3	78.2	6.3	83.2
	78.2		-	6.2			
15	70.3	298	-	4.2		4.2	75.3
16	129.1	298	-	0.8	126.0 ± 3.2	6.5	130.9
	122.8		C	6.5			
17	156.0	298	C	0.3		0.3	161.0
18	111.0	-	MEM	-	128.1 ± 17.1	10.0	133.1
	145.2		ME	10.0			
19	126.4	298	ME	4.4	129.2	10.0	134.2

	132.0		ME	10.0	± 2.8		
20	128.6	298	-	0.9	131.1 ± 4.8	5.2	136.1
	126.4		ME	3.1			
	138.4		C	5.2			
21	73.3	298	C	0.1	73.2 ± 1.6	2.0	78.2
	74.3		ME	0.4			
	73.2		C	0.7			
	72.5	296	ME	1.0			
	72.4	298	-	1.0			
	70.3		ME	1.0			
	72.1	294	ME	0.4			
	71.9	298	-				
	75.6		TE, ME, DM	0.4			
	72.6		ME	1.4			
	73.6		-	0.4			
	74.1		TCM	1.7			
	72.7		ME	2.0			
	76.6		ME	1.0			
22	68.9	298	-	2.0	70.4 ± 1.1	4.2	75.3
	70.0		C	2.0			
	69.5		C	-			
	72.0		-	4.2			
	71.5		BG	0.8			
23	112.0	298	-	4.0		4.0	117.0
24	130.2	298	-	0.7	129.7 ± 1.7	1.5	134.7
	130.6		-	1.5			
	131.7		-	1.3			
	126.4		-	1.1			
25	148.0	-	C	5.0	145.7 ± 2.3	5.0	150.7
	143.4	460	-	2.1			

26	130.1	298	ME	6.3	124.4 ± 5.7	6.3	129.4
	118.7		-	2.2			
27	135.6	298	-	1.0	134.2 ± 1.5	2.5	139.1
	132.7		C	2.5			
28	70.2	298	-	1.5	71.3 ± 1.1	1.5	76.3
	72.4		MM	1.3			
29	157.3	-	C	6.0	153.7 ± 2.4	6.0	158.7
	152.0	549	-	0.8			
	151.9	-	-	2.1			
30	112.0	298	-	29.0		29.0	117.0
31	115.9	298	-	2.4	115.0 ± 2.0	3.0	119.9
	117.0		-	1.6			
	112.0		C	3.0			
32	139.9	463	-	2.1	145.9 ± 6.0	2.1	150.9
	151.9	-	GC	2.1			
33	122.7	298	-	8.6	127.4 ± 4.7	17.0	132.3
	132.0		-	17.0			
34	82.7	298	-	1.7		1.7	87.7
35	77.7	-	-	-	72.6 ± 2.7	1.0	77.5
	69.1	331	-	-			
	76.9	263	ME	0.9			
	73.8	-	-	1.0			
	69.7	363	-	-			
	72.5	-	-	-			
	72.8		-	-			
	68.2		-	-			
36	81.4	-	ME	1.0	87.0 ± 5.6	2.1	91.9
	92.5		-	2.1			
37	168.0	298	-	4.0		4.0	173.0
38	110.2	298	ME	2.9	108.5	2.9	113.4

	106.7		-	2.1	± 1.8		
39	73.2	298	C	4.2		4.2	78.2
40	129.3	-	GS	0.8	129.9 ± 0.6	3.4	134.9
	130.5		ME	3.4			
41	129.7	-	GS	3.8	127.2 ± 2.5	3.8	132.2
	124.7		GS	3.8			
42	96.2	298	-	2.1		2.1	101.2
43	80.5	298	-	1.7		1.7	85.5

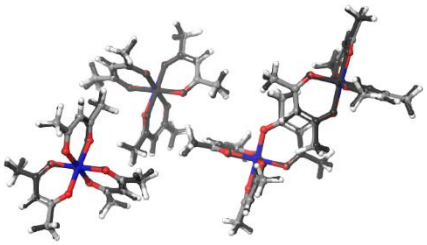
[a] Temperature of measurement for calorimetric measurements or the mean temperature of measurement for experiments conducted over narrow ranges of temperature.

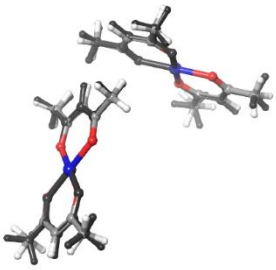
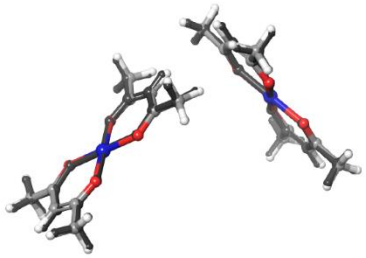
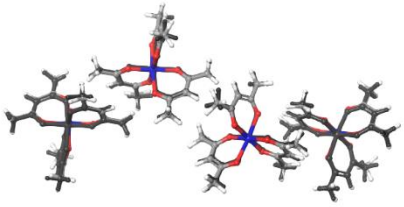
[b] BG = Bourdon gauge, C = calorimetric determination, DM = diaphram manometer, E = estimated, GC = gas chromatography, GS = gas saturation-transpiration, HSA = head space analysis, ME = mass effusion–Knudsen effusion, MEM = modified entrainment method, MM = mercury manometer, TCM = thermal conductivity manometer, TE = torsion effusion.

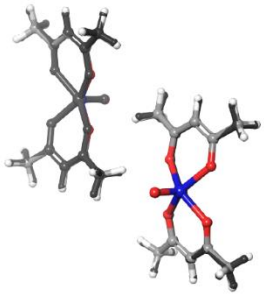
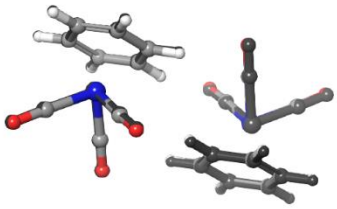
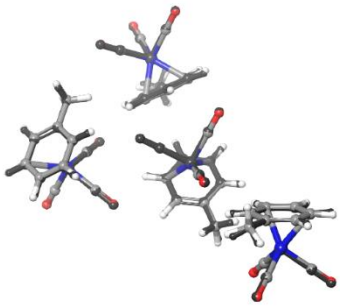
[c] Experimental error if given in original publication.

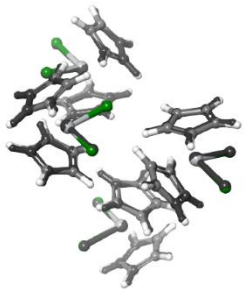
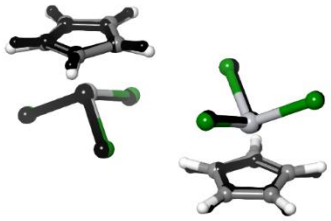
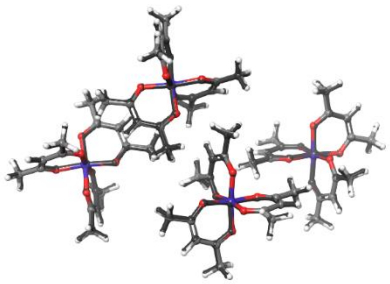
[d] Average experimental heat of sublimation and average deviation of each data point.

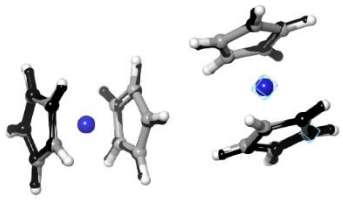
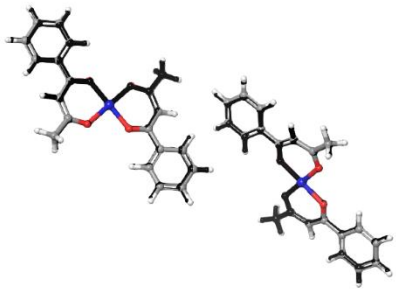
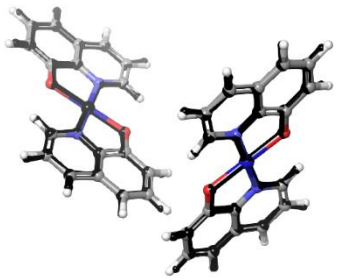
Table S4. Superposition of X-ray single crystal and PBE-D3(BJ)/def2-TZVP optimized structures from periodic DFT calculations. Root mean square deviations between X-ray single crystal structures and optimized PBE-D3(BJ)/def2-TZVP and PBE-D3(BJ)/def2-TZVPP structures.

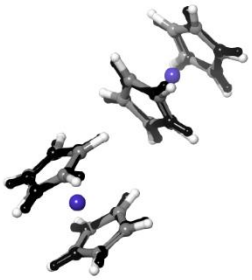
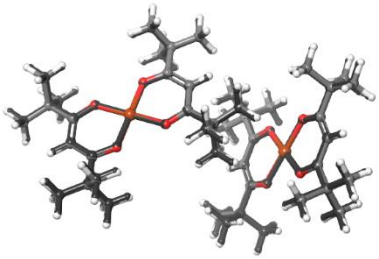
Entry	**CCDC**	**Superposition** **Xray (dark grey) and** **PBE-D3(BJ)/def2-TZVP (in colour)**[a]	**RMSD (Å)**	
			def2-TZVP	***def2-TZVPP***
1	ACACCR07		0.169	0.161

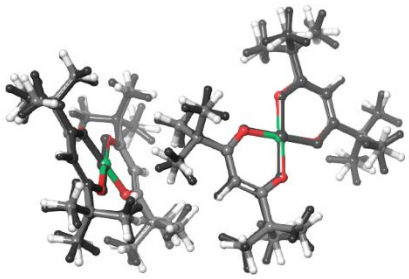
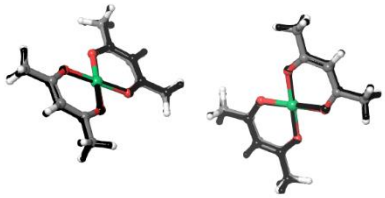
2	ACACS		0.322	0.311
3	ACACCU02		0.128	0.128
4	ACACCMN21		0.306	0.306

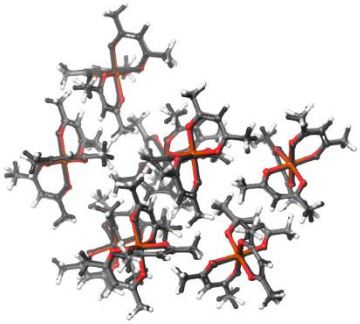
5	ACACVO12		0.131	0.123
6	BZCRCO14		0.038	0.040
7	CCRTOL01		0.116	0.116

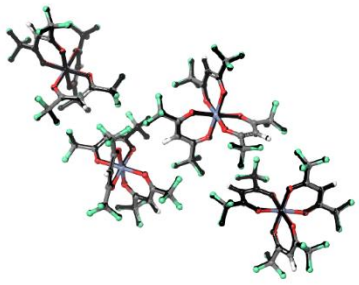
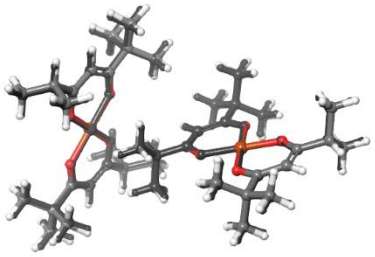
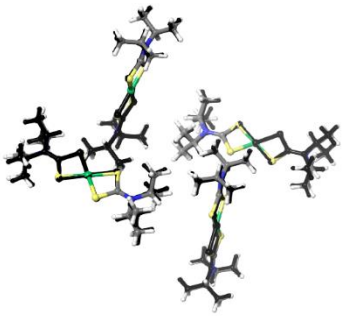
8	CDCPTI04		0.147	0.134
9	CEHPIO01		0.164	0.162
10	COACAC10		0.109	0.108

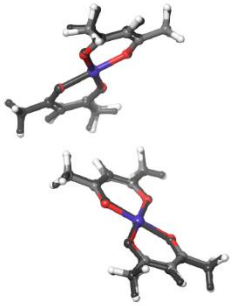
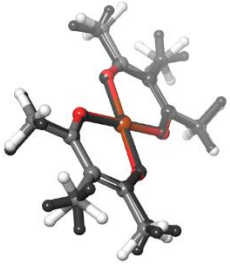
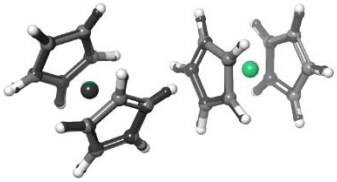
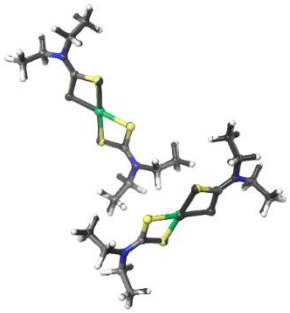
11	CPNDYV07		0.143	0.128
12	CUBEAC01		0.135	0.734
13	CUQUIN05		0.144	0.144

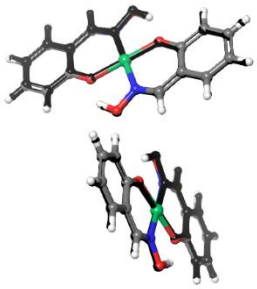
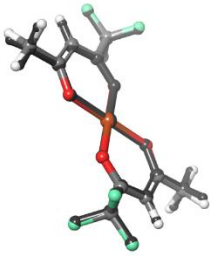
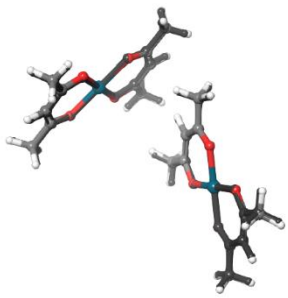
14	DBENCR11		0.080	0.080
15	DCYPCO04		0.250	0.240
16	DERNOD05		0.122	0.121

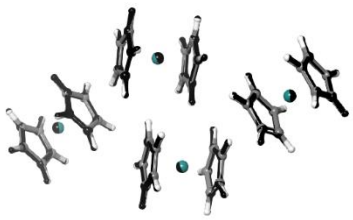
17	DMTCCU		0.260	0.256
18	DPIMNI		0.440	0.441
19	DURHEE		0.182	0.179

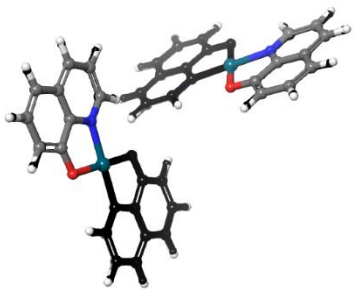
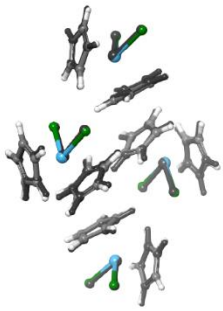
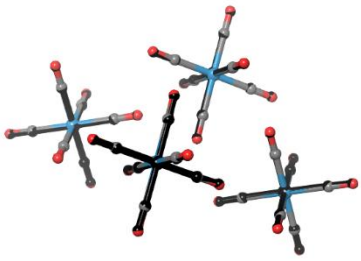
20	FEACAC03		0.335	0.338
21	FEROCE27		0.162	0.161
22	FOHCOU02		0.015	0.017

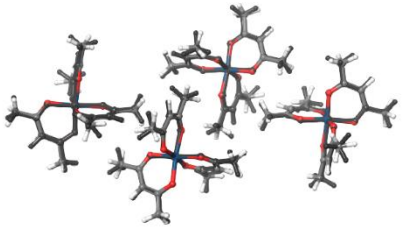
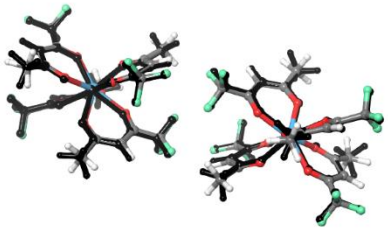
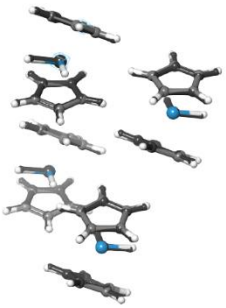
23	IGAGEC		0.072	0.069
24	IPEZOS		0.167	0.166
25	IPTCNI10		0.080	0.080

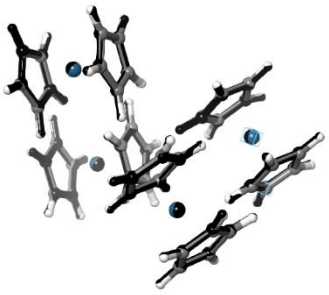
26	LIYLIO		0.144	0.140
27	MACACU10		0.439	0.455
28	NCKLCN01		0.130	0.135
29	NIDCAR06		0.133	0.131

30	NISALO01		0.120	0.119
31	QQQBWP03		0.115	0.115
32	TCBMNI		0.519	0.520
33	ACACPD01		0.113	0.111

34	CYCPRU06		0.024	0.025
35	FUBYIK01		0.009	0.010
36	HCYPMO02		0.050	0.050

37	HQUIPD01		0.106	0.106
38	KOKPEF		0.149	0.141
39	KOVSOD02		0.027	0.028

40	QQQCXJ02		0.429	0.425
41	REGSAY		0.418	0.421
42	REPKIH		0.115	0.114

43	SINWER		0.042	0.041

[a] Display of unit cell omitted for clarity.

Table S5. Final data set of the XTMC43. Experimental and calculated lattice energies in kJ/mol.

XTMC43	**Exp. kJ/mol**	**Calculated kJ/mol**		
Compound ID		**PBE-D3(BJ)/def2-TZVP**	**PBE-D3(BJ)/def2-TZVPP**	**M06-L/def2-TZVPP**
01 (Cr) ACACCR07	128.16	149.70	148.98	127.42
02 (Cr) ACCACS	134.76	143.77	142.47	138.30
03 (Cu) ACACCU02	125.77	141.47	140.19	131.34
04 (Mn) ACACCMN21	127.31	153.52	152.81	128.73
05 (V) ACACVO12	145.36	149.95	148.63	137.96
06 (Cr) BZCRCO14	99.51	99.51	99.16	84.45
07 (Cr) CCRTOL01	98.76	100.91	100.75	88.16
08 (Ti) CDCPTI04	126.56	120.89	120.04	108.12
09 (Ti) CEHPIO01	109.56	95.29	94.89	83.20
10 (Co) COACAC10	139.56	149.36	149.15	135.90
11 (V) CPNDYV07	63.56	87.00	86.25	78.49
12 (Cu) CUBEAC01	164.49	184.80	179.01	159.14
13 (Cu) CUQUIN05	174.31	177.11	175.00	158.13
14 (Cr) DBENCR11	83.16	92.57	91.92	85.42
15 (Co) DCYPCO04	75.26	82.32	81.01	72.36
16 (Cu) DERNOD05	130.91	154.93	154.97	138.34
17 (Cu) DMTCCU	160.96	172.61	172.07	151.34
18 (Ni) DPIMNI	133.06	150.66	150.40	130.43
19 (Ni) DURHEE	134.16	131.80	130.29	119.28
20 (Fe) FEACAC03	136.09	149.29	148.72	127.67
21 (Fe) FEROCE27	78.24	78.11	77.09	62.08
22 (Cr) FOHCOU02	75.34	73.95	73.99	62.79
23 (Cr) IGAGEC	116.96	111.81	111.03	128.22
24 (Cu) IPEZOS	134.68	154.23	153.75	137.49
25 (Ni) IPTCNI10	150.66	180.58	180.41	148.99
26 (Co) LIYLIO	129.36	138.22	135.84	146.24

27 (Cu) MACACU10	139.11	149.76	148.24	137.25
28 (Ni) NCKLCN01	76.26	82.05	80.77	74.89
29 (Ni) NIDCAR06	158.69	177.83	177.11	150.16
30 (Ni) NISALO01	116.96	155.65	152.60	132.39
31 (Cu) QQQBWP03	119.92	132.82	131.62	132.58
32 (Ni) TCBMNI	150.86	178.90	177.90	155.77
33 (Pd) ACACPD01	132.31	133.42	133.02	128.10
34 (Ru) CYCPRU06	87.66	89.81	89.79	75.83
35 (Mo) FUBYIK01	77.54	75.17	75.15	62.22
36 (Mo) HCYPMO02	91.91	99.34	99.37	87.20
37 (Pd) HQUIPD	172.96	175.76	174.45	146.98
38 (Hf) KOKPEF	113.41	113.60	113.62	99.78
39 (W) KOVSOD02	78.16	78.51	78.69	64.79
40 (Ir) QQQCXJ02	134.86	151.39	151.17	129.72
41 (Hf) REGSAY	132.16	148.08	148.40	135.53
42 (W) REPKIH	101.16	102.70	102.20	90.73
43 (Os) SINWER	85.46	94.14	93.56	79.64

Table S6. Bean plot statistics in kJ mol^{-1}.

	Exp.	**PBE-D3(BJ)/def2TZVP**	**PBE-D3(BJ)/def2TZVPP**	**M06L/def2-TZVPP**
Upper whisker	174.31	184.80	180.41	159.14
3rd quartile	135.47	152.45	151.89	137.72
Median	127.31	138.22	135.84	128.22
1st quartile	95.33	97.32	97.03	84.93
Lower whisker	63.56	73.95	73.99	62.08

References

1. F. A. Cotton, C. E. Rice and G. W. Rice, *Inorganica Chimica Acta*, 1977, **24**, 231-234.
2. M. G. Vinum, L. Voigt, S. H. Hansen, C. Bell, K. M. Clark, R. W. Larsen and K. S. Pedersen, *Chemical Science*, 2020, **11**, 8267-8272.