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

Electronic Supplementary Information

Contents

1. Cartesian coordinates of $M(acac)_3$ in the $\mathbf{D}^{SO}$(hybrid CASSCF/MRMP2) principal axes coordinate

In the present study, geometry optimisations were carried out at the UB3LYP/6-31G* level of theory without symmetry constraints by using Gaussian 09. Cartesian coordinates are rotated from the Standard orientations obtained from the geometry optimisations to the principal axes coordinates of the theoretical $\mathbf{D}^{SO}$ tensors calculated at the hybrid CASSCF/MRMP2 method.

Cartesian coordinates of $V(acac)_3$

V	-0.000002	0.000006	0.073106
O	-1.162816	-0.767908	-1.352432
O	1.162819	0.767862	-1.352460
O	1.239488	0.738243	1.489444
O	1.067276	-1.664507	0.168873
O	-1.239518	-0.738173	1.489466
O	-1.067284	1.664524	0.168814
C	-2.085084	-1.415374	-3.426473
C	-1.028918	-0.691874	-2.622204
C	0.000034	-0.000097	-3.281674
C	1.028961	0.691734	-2.622230
C	2.085149	1.415179	-3.426524
C	3.126220	1.179873	2.837744
C	2.363994	0.292054	1.879372
C	2.904035	-0.953834	1.497812
C	2.223084	-1.868587	0.689796
C	2.828099	-3.221194	0.395067
C	-3.126260	-1.179743	2.837786
C	-2.364022	-0.291963	1.879387
C	-2.904056	0.953914	1.497789
C	-2.223094	1.868630	0.689739
C	-2.828105	3.221226	0.394963
H	-2.085994	-2.476082	-3.150880
H	-3.073836	-1.017305	-3.171102
H	-1.928843	-1.324000	-4.504204
H	0.000051	-0.000136	-4.365179
H	3.073897	1.017141	-3.171103
H	1.928946	1.323723	-4.504253
H	2.086040	2.475910	-3.151006
H	2.512188	1.366036	3.726229
H	4.080505	0.744879	3.145042

H	3.307935	2.151104	2.363898
H	3.867429	-1.241548	1.901278
H	2.157017	-4.006378	0.761805
H	2.913485	-3.353957	-0.689598
H	3.812839	-3.347622	0.851741
H	-2.512228	-1.365899	3.726261
H	-4.080534	-0.744721	3.145092
H	-3.308001	-2.150979	2.363957
H	-3.867450	1.241648	1.901247
H	-2.157027	4.006423	0.761678
H	-2.913478	3.353946	-0.689706
H	-3.812850	3.347672	0.851634

Cartesian coordinates of $Cr(acac)_3$

Cr	0.000383	-0.000126	-0.001304
O	1.350306	-0.882077	-1.135762
O	1.426009	0.752371	1.133791
O	-1.359538	0.863054	1.135251
O	0.085695	1.605152	-1.142967
O	-1.435357	-0.731744	-1.137123
O	-0.064556	-1.606777	1.139889
C	3.391058	-1.621715	-2.051007
C	2.620527	-0.845721	-1.006828
C	3.313429	-0.158416	0.002431
C	2.687249	0.593577	1.008983
C	3.525167	1.293763	2.054768
C	-2.871074	2.416408	2.057356
C	-1.853174	2.034038	1.006678
C	-1.521350	2.946486	-0.007082
C	-0.583279	2.686045	-1.018432
C	-0.301910	3.735372	-2.070036
C	-3.090148	-2.133840	-2.055534
C	-2.038671	-1.849941	-1.006708
C	-1.794367	-2.789026	0.007540
C	-0.834365	-2.618616	1.017491
C	-0.653855	-3.688778	2.070225
H	3.146318	-1.231003	-3.045189
H	3.074883	-2.670820	-2.031649
H	4.471812	-1.568496	-1.899315
H	4.395410	-0.210910	0.003911

H	3.313693	2.368791	2.030182
H	4.596341	1.134428	1.909453
H	3.237947	0.932833	3.048815
H	-3.687584	1.685614	2.055898
H	-3.282136	3.416393	1.898965
H	-2.402404	2.372091	3.047060
H	-2.018049	3.909075	-0.008551
H	-0.509500	3.317624	-3.061596
H	0.762332	3.996123	-2.048054
H	-0.896890	4.640958	-1.928888
H	-3.836070	-1.331088	-2.049325
H	-3.591122	-3.092201	-1.898727
H	-2.622175	-2.129451	-3.046506
H	-2.380882	-3.699681	0.010508
H	-0.828301	-3.253769	3.060811
H	0.382689	-4.044120	2.053795
H	-1.327419	-4.537012	1.925969

Cartesian coordinates of $Mn(acac)_3$

Mn	0.052604	-0.000761	-0.000322
O	-1.315257	-1.352176	0.070354
O	0.019587	-0.178836	-2.144068
O	1.436407	1.357348	-0.088150
O	1.408432	-1.386868	0.087783
O	0.023573	0.177693	2.143521
O	-1.287129	1.378692	-0.070864
C	-2.998105	-2.922221	-0.399686
C	-1.949826	-1.945374	-0.883250
C	-1.748320	-1.762820	-2.248616
C	-0.776317	-0.894654	-2.811664
C	-0.660958	-0.806042	-4.321786
C	3.502490	2.480355	-0.176191
C	2.706318	1.200943	-0.082745
C	3.362705	-0.034446	0.001149
C	2.681254	-1.256294	0.083888
C	3.451158	-2.551664	0.177565
C	-0.643176	0.819242	4.321314
C	-0.756941	0.910165	2.811212
C	-1.710461	1.798677	2.248295
C	-1.908513	1.985336	0.882960

C	-2.935880	2.984397	0.399911
H	-2.523348	-3.680271	0.233561
H	-3.728506	-2.394669	0.224360
H	-3.518677	-3.416057	-1.223850
H	-2.370746	-2.334675	-2.926607
H	0.361035	-1.063753	-4.621688
H	-1.364305	-1.460489	-4.843306
H	-0.834902	0.229958	-4.634045
H	3.227808	3.139780	0.654575
H	4.580317	2.303105	-0.156533
H	3.237946	3.002294	-1.102633
H	4.445424	-0.045439	0.001753
H	3.174244	-3.069092	1.102914
H	3.164828	-3.204531	-0.654459
H	4.532391	-2.396277	0.160152
H	0.384329	1.054370	4.620917
H	-1.331806	1.489115	4.842882
H	-0.839868	-0.212622	4.633782
H	-2.320311	2.383835	2.926370
H	-2.445374	3.732012	-0.233739
H	-3.677955	2.472674	-0.223553
H	-3.445078	3.489346	1.224441

Cartesian coordinates of $Fe(acac)_3$

Fe	0.017436	0.000119	0.000011
O	1.382739	0.898529	1.161185
O	0.094752	1.637119	-1.158843
O	-1.439565	-0.753467	-1.157665
O	-1.445558	0.743423	1.156783
O	0.105442	-1.636350	1.158858
O	1.389796	-0.888657	-1.160277
C	2.887005	2.413075	2.167944
C	1.914483	2.054783	1.066417
C	1.657171	2.970917	0.034060
C	0.769373	2.711711	-1.022753
C	0.562299	3.748813	-2.104173
C	-3.501916	-1.358207	-2.133289
C	-2.707931	-0.673493	-1.043038
C	-3.377276	-0.012025	-0.000922
C	-2.713254	0.654319	1.041498

C	-3.512714	1.333304	2.131330
C	0.587013	-3.744833	2.104323
C	0.787531	-2.706256	1.023080
C	1.677779	-2.959223	-0.033182
C	1.929457	-2.041217	-1.065265
C	2.905241	-2.392614	-2.166129
H	2.371192	2.364318	3.133625
H	3.692233	1.670268	2.197014
H	3.319850	3.408503	2.040424
H	2.173300	3.923275	0.050702
H	-0.498931	4.018318	-2.150256
H	1.156341	4.651506	-1.940744
H	0.825081	3.314178	-3.075265
H	-3.221657	-2.416702	-2.176474
H	-4.581271	-1.276724	-1.982258
H	-3.238725	-0.917225	-3.101489
H	-4.460620	-0.015946	-0.001192
H	-3.246661	0.894421	3.099702
H	-3.240300	2.393845	2.174464
H	-4.591377	1.243832	1.979874
H	-0.472372	-4.021587	2.149851
H	1.187300	-4.643427	1.941131
H	0.846330	-3.308489	3.075582
H	2.200514	-3.907974	-0.049555
H	2.389812	-2.347288	-3.132181
H	3.705319	-1.644238	-2.194500
H	3.344889	-3.385036	-2.038435

Cartesian coordinates of $Mo(acac)_3$

Mo	-0.000085	0.000036	0.000685
O	1.711859	0.358510	-1.167105
O	1.232676	-1.243908	1.165236
O	-1.690026	-0.452216	1.168284
O	-0.548510	-1.654263	-1.175846
O	-1.162006	1.309684	-1.164898
O	0.457753	1.681950	1.176581
C	3.890400	0.337367	-2.064695
C	2.892106	-0.116470	-1.022788
C	3.301492	-0.993102	-0.003442
C	2.478691	-1.499013	1.017509

C	3.063163	-2.430727	2.056017
C	-3.630320	-1.450187	2.058249
C	-2.534756	-1.402414	1.016284
C	-2.511317	-2.360878	-0.011298
C	-1.550197	-2.439123	-1.033645
C	-1.659125	-3.524798	-2.081250
C	-2.231192	3.212535	-2.052674
C	-1.341253	2.568346	-1.012814
C	-0.790103	3.354750	0.013324
C	0.055821	2.889396	1.034569
C	0.565829	3.855078	2.081198
H	3.533610	0.046507	-3.059447
H	3.955391	1.431438	-2.055336
H	4.886240	-0.082797	-1.903906
H	4.339106	-1.305518	-0.004842
H	2.520127	-3.382716	2.038876
H	4.127269	-2.622077	1.897481
H	2.919580	-1.998324	3.052848
H	-4.179667	-0.501728	2.053608
H	-4.331595	-2.271783	1.893207
H	-3.180881	-1.554811	3.052430
H	-3.300978	-3.102998	-0.015070
H	-1.725695	-3.065192	-3.074039
H	-0.747941	-4.133944	-2.071092
H	-2.525417	-4.172691	-1.926858
H	-3.213598	2.726512	-2.043235
H	-2.360224	4.285244	-1.889274
H	-1.802821	3.048937	-3.048176
H	-1.038193	4.409606	0.017130
H	0.252702	3.512033	3.074003
H	1.661853	3.855645	2.073834
H	0.205278	4.874536	1.923814

2. CASSCF active space of $M(acac)_3$ (M = Cr, Mn, Fe and Mo)

Note that the CASSCF active space of $V(acac)_3$ is given as Fig. 1 in the text.

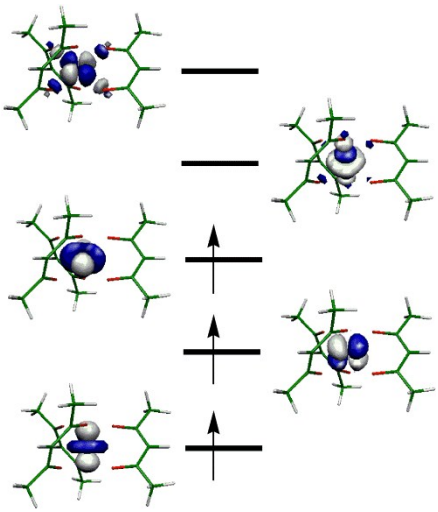

Fig. S1 CASSCF active space and electron occupancies in the main configuration of the ground state of $Cr(acac)_3$.

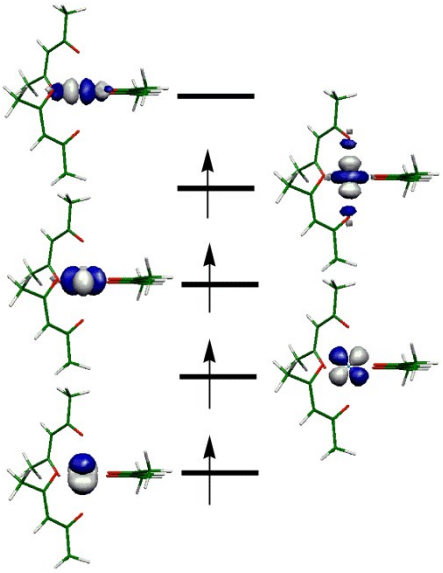

Fig. S2 CASSCF active space and electron occupancies in the main configuration of the ground state of $Mn(acac)_3$.

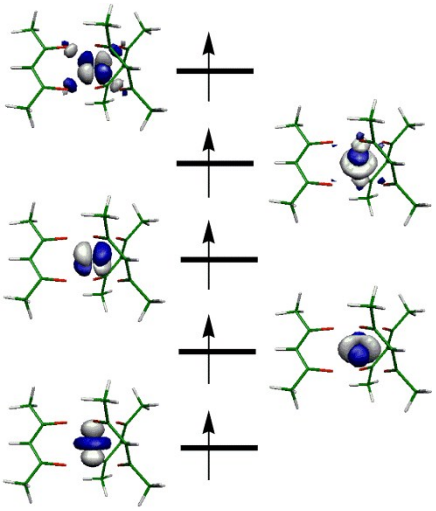

Fig. S3 CASSCF active space and electron occupancies in the main configuration of the ground state of $Fe(acac)_3$.

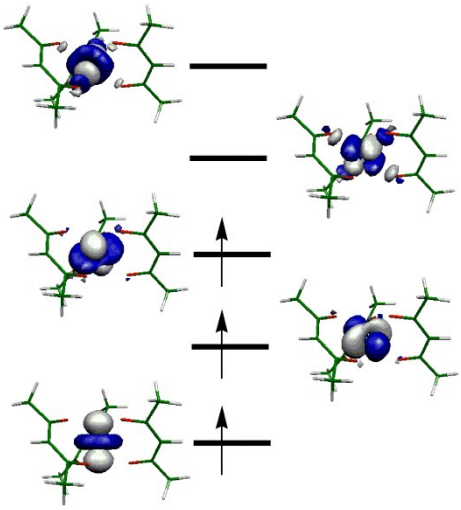

Fig. S4 CASSCF active space and electron occupancies in the main configuration of the ground state of $Mo(acac)_3$.

3. Electronic states of $M(acac)_3$ calculated by using the CASSCF and MRMP2 levels of theory

Table S1 Electronic states of $V(acac)_3$.

State	Main Configurations ($\|C\| > 0.3$)[a]	ΔE_{MRMP2} /cm^{-1}	SOCC[b] /cm^{-1}	$D^{SO}{}_{ii}$[c] /cm^{-1}		
				$i = x$	$i = y$	$i = z$
1 ^{3}A	−0.97 (uu000)					
2 ^{3}A	−0.97 (u0u00)	997	118.78	−1.8658	−12.2832	0.0000
3 ^{3}A	−0.98 (0uu00)	1 643	133.44	−9.2658	−1.5724	0.0000
1 ^{1}A	0.77 (20000) −0.58 (02000)	10 218	26.1	0.0000	0.0000	0.0667
2 ^{1}A	0.74 (00200) −0.55 (02000) −0.32 (20000)	11 928	147.73	0.0000	0.0000	1.8297
3 ^{1}A	−0.97 (ud000)	12 373	2.42	0.0000	0.0000	0.0005
4 ^{1}A	0.81 (u0d00) +0.55 (0ud00)	13 444	103.22	0.0341	0.7583	0.0000
4 ^{3}A	0.75 (u00u0) −0.51 (0u0u0) −0.43 (00u0u)	13 820	183.82	−0.6310	−1.8140	0.0000
5 ^{1}A	−0.81 (0ud00) +0.57 (u0d00)	14 385	136.89	1.2179	0.0847	0.0000
5 ^{3}A	−0.75 (u000u) +0.49 (00uu0) −0.45 (0u00u)	14 503	143.65	0.0000	0.0000	−1.4227
6 ^{3}A	0.71 (0u00u) +0.70 (00uu0)	16 548	102.61	0.0000	0.0000	−0.6362
6 ^{1}A	0.60 (00200) +0.54 (02000) +0.45 (20000)	24 471	121.90	0.0000	0.0000	0.6072
7 ^{3}A	−0.65 (u000u) +0.52 (0u00u) −0.51 (00uu0)	26 220	4.20	0.0000	0.0000	−0.0007
8 ^{3}A	−0.75 (0u0u0) −0.60 (u00u0)	26 356	55.05	−0.0738	−0.0412	0.0000
9 ^{3}A	−0.83 (00u0u) −0.33 (000uu) +0.33 (0u0u0)	27 957	39.80	−0.0229	−0.0337	0.0000
7 ^{1}A	0.79 (u000d) −0.49 (00ud0) +0.31 (0u00d)	29 254	99.31	0.0000	0.0000	0.3371
8 ^{1}A	−0.83 (u00d0) +0.44 (0u0d0)	29 257	155.40	0.1252	0.7002	0.0000
9 ^{1}A	0.73 (0u00d) +0.65 (00ud0)	30 576	76.70	0.0000	0.0000	0.1924
10 ^{1}A	0.59 (u000d) −0.58 (0u00d) +0.56 (00ud0)	33 381	15.26	0.0000	0.0000	0.0070
11 ^{1}A	0.87 (0u0d0) +0.49 (u00d0)	34 011	107.80	0.2880	0.0537	0.0000
12 ^{1}A	0.96 (00u0d)	34 795	71.36	0.0514	0.0949	0.0000
10 ^{3}A	0.94 (000uu)	34 809	13.68	−0.0041	−0.0013	0.0000
13 ^{1}A	−0.73 (00020) +0.68 (00002)	48 887	16.83	0.0000	0.0000	0.0058
14 ^{1}A	−0.99 (000ud)	49 055	25.86	0.0083	0.0053	0.0000
15 ^{1}A	0.69 (00002) +0.62 (00020)	63 098	7.25	0.0000	0.0000	0.0008

[a] 2, 0, u, and d stand for the doubly occupied, unoccupied, spin up (α), and spin down (β), respectively. [b] Spin–orbit coupling constants. [c] Contributions to the $\mathbf{D}^{SO}$ principal values.

Table S2 Electronic states of $Cr(acac)_3$

State	Main Configurations ($\|C\| > 0.3$)[a]	ΔE_{MRMP2} /cm^{-1}	SOCC[b] /cm^{-1}	$D^{SO}{}_{ii}{}^{c}$/cm^{-1}		
				$i = x$	$i = y$	$i = z$
1 ^{4}A	1.00 (uuu00)					
2 ^{4}A	−0.68 (0uu0u) −0.48 (uu00u) −0.47 (u0uu0)	15 372	244.59	−0.1388	−1.5908	0.0000
3 ^{4}A	−0.68 (0uuu0) +0.48 (uu0u0) −0.48 (u0u0u)	15 398	244.62	−1.5887	−0.1385	0.0000
4 ^{4}A	0.71 (u0uu0) −0.71 (uu00u)	16 324	254.82	0.0000	0.0000	−1.7678
1 ^{2}A	−0.60 (20u00) +0.57 (02u00) −0.32 (u2000) +0.32 (u0200)	17 836	8.51	0.0001	0.0020	0.0000
2 ^{2}A	−0.60 (2u000) −0.57 (0u200) −0.39 (uud00)	17 839	8.57	0.0020	0.0001	0.0000
3 ^{2}A	−0.85 (udu00) +0.49 (uud00)	18 747	0.08	0.0000	0.0000	0.0000
4 ^{2}A	0.61 (u2000) −0.61 (u0200) −0.32 (20u00) +0.31 (02u00)	19 019	0.64	0.0000	0.0000	0.0000
5 ^{2}A	−0.75 (uud00) −0.43 (udu00) +0.32 (2u000) +0.31 (0u200)	19 033	0.52	0.0000	0.0000	0.0000
6 ^{2}A	0.63 (0u200) −0.58 (2u000)	22 594	275.17	1.6690	0.0067	0.0000
7 ^{2}A	−0.63 (02u00) −0.58 (20u00)	22 776	275.23	0.0067	1.6563	0.0000
5 ^{4}A	−0.61 (0uuu0) +0.49 (00uuu) −0.42 (uu0u0) +0.42 (u0u0u)	23 611	3.12	−0.0002	0.0000	0.0000
6 ^{4}A	0.61 (0uu0u) +0.49 (0u0uu) −0.42 (uu00u) −0.42 (u0uu0)	23 613	3.23	0.0000	−0.0002	0.0000
8 ^{2}A	0.61 (u0200) +0.61 (u2000)	23 973	249.10	0.0000	0.0000	1.2941
7 ^{4}A	−0.60 (u0u0u) −0.60 (uu0u0) +0.53 (u00uu)	24 890	0.11	0.0000	0.0000	0.0000
9 ^{2}A	0.56 (002u0) +0.48 (ud00u) +0.48 (u0du0) −0.43 (0ud0u)	31 421	5.16	0.0000	0.0004	0.0000
10 ^{2}A	0.59 (u0du0) −0.58 (ud00u) +0.38 (0ud0u)	32 090	0.39	0.0000	0.0000	0.0000
11 ^{2}A	−0.50 (200u0) +0.38 (002u0) −0.34 (ud00u) −0.34 (u0du0) −0.32 (0uu0d)	33 280	25.05	0.0008	0.0087	0.0000
12 ^{2}A	−0.50 (2000u) +0.38 (0200u) −0.34 (ud0u0) +0.34 (u0d0u) +0.32 (0uud0)	33 597	24.42	0.0080	0.0009	0.0000
13 ^{2}A	−0.58 (0uu0d) −0.43 (uu00d) −0.43 (u0ud0)	34 247	178.66	0.0343	0.4318	0.0000
14 ^{2}A	−0.58 (0uud0) +0.43 (uu0d0) −0.43 (u0u0d)	34 266	178.79	0.4322	0.0342	0.0000
15 ^{2}A	0.63 (u0ud0) −0.63 (uu00d)	34 283	196.56	0.0000	0.0000	0.5635
16 ^{2}A	−0.56 (0200u) +0.48 (u0d0u) −0.48 (ud0u0) +0.43 (0udu0)	35 833	5.23	0.0004	0.0000	0.0000
17 ^{2}A	−0.49 (0udu0) −0.37 (u0d0u) −0.37 (ud0u0) +0.35 (0020u) −0.32 (u0u0d) −0.31 (uu0d0)	35 963	0.57	0.0000	0.0000	0.0000
8 ^{4}A	−0.85 (u00uu) −0.38 (uu0u0)	38 957	0.04	0.0000	0.0000	0.0000

	−0.38 (u0u0u)					
18 ^{2}A	−0.59 (0uu0d) +0.43 (uu00d) +0.43 (u0ud0)	40 015	3.66	0.0000	0.0002	0.0000
19 ^{2}A	0.59 (0uud0) +0.43 (uu0d0) −0.42 (u0u0d)	40 255	3.77	0.0002	0.0000	0.0000
9 ^{4}A	−0.86 (0u0uu) +0.36 (0uu0u)	40 837	1.47	0.0000	0.0000	0.0000
10 ^{4}A	0.86 (00uuu) +0.36 (0uuu0)	40 924	1.44	0.0000	0.0000	0.0000
20 ^{2}A	0.59 (u0u0d) +0.58 (uu0d0)	41 181	0.12	0.0000	0.0000	0.0000
21 ^{2}A	0.47 (0u002) −0.41 (2000u) +0.35 (0020u)	48 064	14.48	0.0021	0.0000	0.0000
22 ^{2}A	−0.45 (00u20) −0.41 (200u0) +0.33 (020u0)	48 110	14.53	0.0000	0.0021	0.0000
23 ^{2}A	0.36 (0ud0u) −0.34 (u0020) +0.30 (020u0)	48 410	19.17	0.0000	0.0000	0.0038
24 ^{2}A	−0.54 (u0d0u) −0.54 (ud0u0) +0.40 (0udu0)	50 807	0.01	0.0000	0.0000	0.0000
25 ^{2}A	0.74 (u00du) −0.43 (u00ud)	52 331	0.05	0.0000	0.0000	0.0000
26 ^{2}A	−0.41 (00u20) +0.35 (0u0du) +0.33 (200u0) −0.32 (u0020) +0.32 (u0002)	53 637	58.30	0.0005	0.0312	0.0000
27 ^{2}A	0.61 (00udu) −0.55 (00uud) −0.45 (u00ud)	53 939	11.52	0.0012	0.0000	0.0000
28 ^{2}A	−0.44 (00uud) +0.41 (0u002) +0.40 (u00ud) +0.33 (2000u)	53 978	58.30	0.0310	0.0005	0.0000
29 ^{2}A	−0.78 (0u0du) +0.37 (u0002) −0.37 (u0020)	54 045	11.54	0.0000	0.0012	0.0000
30 ^{2}A	−0.46 (0u0ud) −0.37 (00u20) +0.37 (00u02) +0.32 (0ud0u)	55 078	61.12	0.0000	0.0000	0.0339
31 ^{2}A	−0.67 (0002u) +0.51 (0020u) +0.30 (2000u)	59 204	5.68	0.0003	0.0000	0.0000
32 ^{2}A	0.67 (000u2) +0.51 (020u0) +0.30 (200u0)	59 497	5.63	0.0000	0.0003	0.0000
33 ^{2}A	−0.60 (00udu) −0.47 (00uud) −0.43 (u00du)	61 810	1.97	0.0000	0.0000	0.0000
34 ^{2}A	0.49 (0u002) −0.48 (u00ud) −0.44 (0u020) −0.32 (00udu)	62 238	2.63	0.0001	0.0000	0.0000
35 ^{2}A	−0.57 (0u0ud) +0.36 (u0002) −0.36 (u0020) +0.32 (00u20)	62 252	3.27	0.0000	0.0001	0.0000
36 ^{2}A	−0.70 (0002u) −0.51 (0020u) −0.35 (2000u)	75 373	3.49	0.0001	0.0000	0.0000
37 ^{2}A	0.70 (000u2) −0.41 (020u0) −0.35 (200u0)	75 774	3.46	0.0000	0.0001	0.0000
38 ^{2}A	0.73 (00u02) +0.44 (00u20)	76 794	13.56	0.0000	0.0012	0.0000
39 ^{2}A	−0.73 (0u020) −0.44 (0u002)	76 932	13.55	0.0012	0.0000	0.0000
40 ^{2}A	0.60 (u0020) +0.60 (u0002)	78 206	6.64	0.0000	0.0000	0.0003

[a] 2, 0, u, and d stand for the doubly occupied, unoccupied, spin up (α), and spin down (β), respectively. [b] Spin–orbit coupling constants. [c] Contributions to the $\mathbf{D}^{SO}$ principal values.

Table S3 Electronic states of $Mn(acac)_3$.

State	Main Configurations ($\|C\| > 0.3$)[a]	ΔE_{MRMP2} /cm^{-1}	SOCC[b] /cm^{-1}	$D^{SO}{}_{ii}{}^{c}$ /cm^{-1}		
				$i = x$	$i = y$	$i = z$
1 ^{5}A	1.00 (uuuu0)					
2 ^{5}A	−1.00 (uuu0u)	8 885	31.42	0.0000	−0.0125	−0.0153
1 ^{3}A	0.95 (uu200)	10 742	45.86	0.0653	0.0000	0.0000
2 ^{3}A	0.96 (2uu00)	10 772	274.98	2.3396	0.0002	0.0000
3 ^{3}A	0.97 (u2u00)	11 388	282.82	0.0002	2.3346	0.0064
4 ^{3}A	0.66 (u02u0) −0.53 (20uu0) +0.34 (02uu0)	16 300	142.68	0.0000	0.4087	0.0076
5 ^{3}A	−0.85 (0u2u0) −0.33 (uudu0) −0.30 (2u0u0)	17 809	164.66	0.5074	0.0001	0.0000
3 ^{5}A	−1.00 (uu0uu)	19 192	318.67	0.0000	−0.0080	−1.3148
4 ^{5}A	−1.00 (u0uuu)	20 819	160.65	−0.3099	0.0000	0.0000
6 ^{3}A	0.85 (u200u)	21 666	114.01	0.2000	0.0000	0.0000
5 ^{5}A	1.00 (0uuuu)	21 696	166.75	0.0000	−0.2889	−0.0315
7 ^{3}A	0.84 (uuud0) −0.46 (uudu0)	22 667	2.96	0.0001	0.0000	0.0000
8 ^{3}A	−0.64 (2u00u) +0.54 (udu0u) +0.31 (02uu0)	22 919	146.84	0.0000	0.1203	0.1932
9 ^{3}A	0.58 (u02u0) −0.47 (02uu0) +0.41 (20uu0) +0.38 (uuu0d)	22 970	72.23	0.0000	0.0753	0.0004
10 ^{3}A	−0.91 (uduu0)	23 172	34.98	0.0176	0.0000	0.0000
11 ^{3}A	0.59 (2u00u) +0.50 (udu0u) +0.34 (20uu0) +0.31 (02uu0)	25 662	167.47	0.0000	0.0235	0.3408
12 ^{3}A	−0.73 (uudu0) −0.44 (uuud0)	26 955	13.60	0.0023	0.0000	0.0000
13 ^{3}A	0.78 (u0u20) +0.33 (0uuud)	30 168	348.02	0.0002	1.3381	0.0000
14 ^{3}A	−0.57 (200uu) +0.38 (u0duu) +0.36 (2u0u0) +0.35 (020uu)	30 683	54.92	0.0328	0.0000	0.0000
15 ^{3}A	0.74 (0uu20) +0.40 (u0uud)	31 078	352.42	1.3319	0.0002	0.0000
16 ^{3}A	0.65 (uuu0d) +0.62 (uud0u) +0.32 (02uu0)	31 472	18.58	0.0000	0.0011	0.0026
17 ^{3}A	0.59 (02u0u) −0.57 (20u0u) +0.31 (uuud0)	33 986	9.45	0.0009	0.0000	0.0000
18 ^{3}A	0.52 (u0duu) −0.41 (020uu) +0.32 (02u0u)	35 337	0.40	0.0000	0.0000	0.0000
19 ^{3}A	−0.59 (0uduu) −0.39 (u20u0) +0.33 (0uudu) −0.33 (uu0du)	35 893	101.29	0.0000	0.0003	0.0950
20 ^{3}A	−0.62 (uud0u) +0.58 (uuu0d) −0.35 (ud0uu)	36 118	70.27	0.0000	0.0103	0.0352
21 ^{3}A	−0.74 (uu0du) +0.33 (0uduu)	37 392	142.85	0.0000	0.0334	0.1485
22 ^{3}A	0.66 (0uuud) −0.60 (0uudu)	39 983	113.95	0.0000	0.1080	0.0002
23 ^{3}A	0.76 (uu002) −0.47 (uu020)	40 951	4.35	0.0002	0.0000	0.0000
24 ^{3}A	0.69 (u0uud) −0.59 (u0udu)	41 099	81.97	0.0545	0.0000	0.0000
25 ^{3}A	0.71 (002uu) −0.44 (020uu)	43 622	10.79	0.0009	0.0000	0.0000
26 ^{3}A	0.61 (u002u) −0.38 (u020u) +0.37 (u0udu)	44 023	0.78	0.0000	0.0000	0.0000
27 ^{3}A	−0.49 (0u02u) +0.40 (0uudu)	44 071	50.38	0.0000	0.0000	0.0192
28 ^{3}A	0.53 (0u20u) −0.44 (0uuud)	44 864	51.88	0.0000	0.0183	0.0017

	+0.32 (u20u0)					
29 ^{3}A	0.55 (udu0u) −0.39 (20uu0) −0.33 (02uu0) +0.30 (00uu2)	45 226	137.15	0.0000	0.0028	0.1358
30 ^{3}A	−0.64 (00u2u)	45 363	35.71	0.0094	0.0000	0.0000
31 ^{3}A	0.40 (u0uud) −0.40 (00u2u) +0.37 (u0duu) +0.32 (u0udu)	45 992	59.12	0.0253	0.0000	0.0000
32 ^{3}A	0.80 (ud0uu) −0.31 (uud0u)	46 075	36.55	0.0000	0.0013	0.0083
33 ^{3}A	0.86 (uu0ud) +0.34 (uu0du)	46 371	242.71	0.0000	0.0033	0.4202
34 ^{3}A	−0.58 (0u0u2) −0.40 (u002u) −0.38 (u0duu)	51 339	6.18	0.0002	0.0000	0.0000
35 ^{3}A	0.60 (u00u2) −0.45 (0uduu) +0.40 (0u02u)	52 198	26.85	0.0000	0.0000	0.0046
36 ^{3}A	−0.36 (uu020) −0.35 (0u0u2) −0.34 (uu002) +0.34 (20u0u) +0.32 (0uu02)	62 014	7.20	0.0003	0.0000	0.0000
37 ^{3}A	−0.58 (uu020) −0.44 (uu002) +0.37 (0u0u2)	62 597	2.96	0.0000	0.0000	0.0000
38 ^{3}A	−0.58 (u00u2) +0.41 (u20u0) −0.37 (0uduu) −0.34 (0u20u)	64 037	5.30	0.0000	0.0001	0.0000
39 ^{3}A	−0.48 (00u2u) +0.38 (02u0u) +0.36 (20u0u) +0.34 (uu020) +0.32 (u020u)	65 536	11.17	0.0006	0.0000	0.0000
40 ^{3}A	0.53 (u002u) +0.43 (u020u) −0.32 (u0udu)	65 695	33.81	0.0058	0.0000	0.0000
41 ^{3}A	0.68 (0u02u) +0.45 (0u20u) +0.33 (0uudu) −0.32 (u00u2)	67 839	24.18	0.0000	0.0017	0.0001
42 ^{3}A	0.56 (002uu) +0.51 (020uu) +0.45 (200uu)	69 349	8.74	0.0004	0.0000	0.0000
43 ^{3}A	−0.59 (00uu2) −0.58 (u0u02)	71 819	63.12	0.0000	0.0185	0.0000
44 ^{3}A	0.65 (00uu2) −0.59 (u0u02)	75 326	92.73	0.0380	0.0000	0.0000
45 ^{3}A	−0.74 (0uu02) −0.50 (0u0u2)	76 205	74.47	0.0000	0.0243	0.0000

[a] 2, 0, u, and d stand for the doubly occupied, unoccupied, spin up (α), and spin down (β), respectively. [b] Spin–orbit coupling constants. [c] Contributions to the $\mathbf{D}^{SO}$ principal values.

Table S4 Electronic states of $Fe(acac)_3$.

State	Main Configurations ($\|C\| > 0.3$)[a]	ΔE_{MRMP2} /cm^{-1}	SOCC[b] /cm^{-1}	$D^{SO}{}_{ii}{}^{c}$ /cm^{-1}		
				$i = x$	$i = y$	$i = z$
1 ^{6}A	1.00 (uuuuu)					
1 ^{4}A	0.72 (2uu0u) +0.47 (uu2u0) +0.46 (u2u0u)	18 714	377.00	1.8986	0.0000	0.0000
2 ^{4}A	−0.70 (2uuu0) +0.50 (u2uu0) −0.46 (uu20u)	18 762	376.41	0.0000	1.8877	0.0002
3 ^{4}A	0.70 (uu20u) +0.69 (u2uu0)	22 005	384.13	0.0000	0.0002	1.6762
4 ^{4}A	−0.56 (2uuu0) +0.43 (uu20u) −0.42 (u2uu0)	23 898	11.80	0.0000	0.0014	0.0000
5 ^{4}A	0.54 (2uu0u) −0.45 (uu2u0) −0.43 (u2u0u) −0.32 (uuduu)	24 055	11.23	0.0013	0.0000	0.0000
6 ^{4}A	0.57 (u2u0u) −0.55 (uu2u0) −0.44 (uduuu)	26 067	0.05	0.0000	0.0000	0.0000
7 ^{4}A	−0.78 (uuudu) +0.60 (uuuud)	33 022	0.08	0.0000	0.0000	0.0000
8 ^{4}A	0.49 (uuu20) −0.49 (uuu02) +0.45 (2u0uu) +0.41 (0u2uu)	33 126	6.59	0.0000	0.0003	0.0000
9 ^{4}A	−0.55 (uuuud) −0.43 (20uuu) −0.43 (uuudu) −0.39 (02uuu) −0.35 (uuduu)	33 141	5.89	0.0003	0.0000	0.0000
10 ^{4}A	−0.73 (uduuu) +0.42 (uuduu) +0.37 (uu2u0) −0.36 (u2u0u)	36 265	2.33	0.0000	0.0000	0.0000
11 ^{4}A	−0.49 (u20uu) +0.49 (u02uu) +0.41 (2u0uu) +0.35 (2uuu0) +0.35 (0u2uu)	36 331	12.57	0.0000	0.0011	0.0000
12 ^{4}A	−0.59 (uuduu) −0.43 (20uuu) +0.37 (02uuu) −0.34 (2uu0u) −0.30 (uduuu)	36 382	13.32	0.0012	0.0000	0.0000
13 ^{4}A	−0.50 (uuu20) +0.50 (uuu02) +0.43 (2u0uu) −0.34 (u02uu) +0.33 (u20uu)	39 624	71.53	0.0000	0.0323	0.0000
14 ^{4}A	−0.56 (uuuud) −0.43 (uuudu) +0.41 (uuduu) −0.41 (20uuu)	39 690	70.50	0.0313	0.0000	0.0000
15 ^{4}A	−0.54 (0uu2u) +0.49 (02uuu) +0.42 (uu0u2) +0.40 (u0u2u) +0.34 (20uuu)	42 892	508.99	1.5100	0.0000	0.0000
16 ^{4}A	0.52 (0uuu2) −0.49 (0u2uu) −0.44 (uu02u) +0.40 (u0uu2) +0.34 (2u0uu)	44 194	509.25	0.0000	1.4641	0.0029
17 ^{4}A	0.63 (u0uu2) +0.59 (uu02u) +0.34 (u02uu) +0.34 (u20uu)	46 922	508.82	0.0000	0.0028	1.3767
18 ^{4}A	−0.70 (uuu02) −0.70 (uuu20)	50 908	16.60	0.0000	0.0000	0.0014
19 ^{4}A	0.61 (u02uu) +0.61 (u20uu) −0.34 (uu02u) −0.33 (u0uu2)	54 981	65.72	0.0000	0.0000	0.0196
20 ^{4}A	−0.58 (02uuu) −0.53 (20uuu) −0.34 (0uu2u) +0.34 (uu0u2) +0.33 (u0u2u)	55 371	73.57	0.0244	0.0000	0.0000

21 ^{4}A	−0.57 (0u2uu) +0.53 (2u0uu) −0.35 (u0uu2) +0.34 (uu02u) −0.33 (0uuu2)	55 835	73.09	0.0000	0.0239	0.0000
22 ^{4}A	0.74 (0uuu2) +0.42 (uu02u) −0.40 (u0uu2)	59 131	19.50	0.0000	0.0016	0.0000
23 ^{4}A	0.72 (0uu2u) +0.44 (uu0u2) +0.42 (u0u2u)	59 381	19.46	0.0016	0.0000	0.0000
24 ^{4}A	0.68 (u0u2u) −0.65 (uu0u2)	60 340	0.22	0.0000	0.0000	0.0000

[a] 2, 0, u, and d stand for the doubly occupied, unoccupied, spin up (α), and spin down (β), respectively. [b] Spin–orbit coupling constants. [c] Contributions to the $\mathbf{D}^{SO}$ principal values.

Table S5 Electronic states of $Mo(acac)_3$.

State	Main Configurations ($\|C\| > 0.3$)[a]	ΔE_{MRMP2} /cm^{-1}	SOCC[b] /cm^{-1}	$D^{SO}{}_{ii}{}^{c}$ /cm^{-1}		
				$i = x$	$i = y$	$i = z$
1 ^{4}A	−1.00 (uuu00)					
1 ^{2}A	0.65 (20u00) −0.51 (02u00)	12 094	74.80	0.0131	0.2182	0.0000
2 ^{2}A	0.65 (2u000) +0.51 (0u200) +0.33 (uud00)	12 156	75.17	0.2192	0.0133	0.0000
3 ^{2}A	−0.87 (udu00) +0.49 (uud00)	12 960	0.50	0.0000	0.0000	0.0000
4 ^{2}A	−0.77 (uud00) −0.44 (udu00)	13 448	38.52	0.0506	0.0045	0.0000
5 ^{2}A	0.63 (u2000) −0.63 (u0200)	13 477	38.50	0.0044	0.0506	0.0000
6 ^{2}A	−0.71 (02u00) −0.54 (20u00)	17 702	663.82	8.6577	3.7886	0.0001
7 ^{2}A	−0.71 (0u200) +0.54 (2u000)	17 709	663.57	3.7845	8.6473	0.0001
8 ^{2}A	0.68 (u0200) +0.68 (u2000)	19 270	532.78	0.0000	0.0001	7.3652
2 ^{4}A	0.68 (uu0u0) −0.67 (u0u0u)	25 297	746.57	−0.0001	−0.0010	−9.7912
3 ^{4}A	0.64 (0uuu0) +0.54 (u0u0u) +0.52 (uu0u0)	25 984	699.14	−0.3765	−7.9830	−0.0013
4 ^{4}A	−0.63 (0uu0u) −0.53 (u0uu0) +0.53 (uu00u)	26 021	699.01	−7.9693	−0.3763	0.0000
5 ^{4}A	−0.75 (0uuu0) +0.42 (u0u0u) +0.42 (uu0u0)	32 172	50.12	−0.0025	−0.0322	0.0000
6 ^{4}A	0.67 (uu00u) +0.65 (u0uu0)	32 179	0.29	0.0000	0.0000	0.0000
7 ^{4}A	0.76 (0uu0u) −0.44 (u0uu0) +0.41 (uu00u)	32 254	51.52	−0.0339	−0.0026	0.0000
9 ^{2}A	−0.65 (200u0) +0.35 (u0du0) −0.34 (ud00u) −0.32 (u0ud0) +0.31 (uu00d)	35 022	229.18	0.6991	0.0507	0.0001
10 ^{2}A	−0.64 (2000u) +0.43 (u0u0d) −0.35 (u0d0u) −0.33 (ud0u0)	35 582	254.98	0.0476	0.6689	0.1971
11 ^{2}A	0.59 (ud0u0) −0.59 (u0d0u)	36 426	53.30	0.0000	0.0000	0.0390
12 ^{2}A	0.69 (uu0d0) −0.57 (u0u0d)	37 758	634.25	0.0016	0.0243	5.3011
13 ^{2}A	0.64 (0uu0d) +0.40 (u0ud0) −0.39 (uu00d)	38 722	539.37	3.5637	0.1929	0.0000
14 ^{2}A	−0.64 (0uud0) −0.40 (u0u0d) −0.39 (uu0d0)	38 743	539.21	0.1930	3.5592	0.0001
15 ^{2}A	0.59 (0020u) −0.42 (0udu0) +0.35 (u0d0u) +0.35 (ud0u0)	39 065	47.48	0.0045	0.0243	0.0000
16 ^{2}A	−0.39 (ud00u) −0.39 (0ud0u) −0.37 (u0du0) −0.33 (uu00d) −0.32 (u0ud0)	39 381	10.29	0.0011	0.0002	0.0000
17 ^{2}A	0.59 (020u0) −0.42 (0ud0u) −0.35 (u0du0) +0.35 (ud00u)	39 773	48.86	0.0255	0.0045	0.0000
18 ^{2}A	−0.61 (u0ud0) −0.55 (uu00d)	42 517	1.81	0.0000	0.0000	0.0000
19 ^{2}A	−0.66 (0uu0d) −0.46 (uu00d) +0.37 (u0ud0)	42 742	15.57	0.0026	0.0002	0.0000
20 ^{2}A	−0.65 (0uud0) +0.42 (u0u0d) +0.42 (uu0d0)	42 801	14.39	0.0002	0.0022	0.0000
21 ^{2}A	−0.54 (2000u) +0.40 (0200u) +0.37 (0udu0)	45 202	59.12	0.0074	0.0312	0.0000

22 ^{2}A	−0.54 (200u0) +0.40 (002u0) +0.36 (0ud0u)	45 238	59.62	0.0318	0.0075	0.0000
23 ^{2}A	−0.46 (0udu0) −0.34 (0ud0u) +0.34 (0200u) −0.33 (0020u) +0.32 (u0d0u) −0.30 (ud0u0)	46 493	59.48	0.0000	0.0000	0.0380
24 ^{2}A	0.52 (ud00u) +0.52 (u0du0) −0.36 (0ud0u)	47 825	0.01	0.0000	0.0000	0.0000
25 ^{2}A	−0.67 (002u0) −0.46 (020u0) −0.39 (200u0)	54 417	0.85	0.0000	0.0000	0.0000
8 ^{4}A	0.98 (u00uu)	54 447	0.04	0.0000	0.0000	0.0000
26 ^{2}A	−0.67 (0200u) −0.46 (0020u) −0.39 (2000u)	55 288	0.84	0.0000	0.0000	0.0000
9 ^{4}A	0.95 (00uuu)	58 098	5.14	−0.0001	−0.0001	0.0000
10 ^{4}A	−0.95 (0u0uu)	58 098	5.09	−0.0001	−0.0001	0.0000
27 ^{2}A	0.81 (u00du) −0.47 (u00ud)	65 292	0.10	0.0000	0.0000	0.0000
28 ^{2}A	−0.62 (u00ud) −0.53 (00udu) −0.36 (u00du) +0.31 (00uud)	66 076	35.21	0.0065	0.0029	0.0000
29 ^{2}A	−0.53 (0u0du) −0.51 (u0020) +0.51 (u0002) +0.30 (0u0ud)	66 077	35.01	0.0029	0.0064	0.0000
30 ^{2}A	0.67 (0u0ud) −0.52 (00u02)	67 520	53.62	0.0010	0.0203	0.0000
31 ^{2}A	−0.50 (0u0ud) −0.43 (00u02) +0.42 (00u20) −0.33 (u0002) −0.31 (u0020)	67 531	69.98	0.0000	0.0000	0.0363
32 ^{2}A	0.68 (00udu) −0.53 (0u020) −031 (u00ud)	67 720	53.56	0.0202	0.0010	0.0000
33 ^{2}A	−0.64 (00uud) −+0.41 (0u020) −0.41 (u00ud)	71 226	15.44	0.0016	0.0001	0.0000
34 ^{2}A	−0.66 (0u0du) +0.40 (00u02) +0.33 (u0020) −0.33 (u0002)	71 331	15.54	0.0001	0.0016	0.0000
35 ^{2}A	−0.55 (00uud) −0.43 (0u002) +0.43 (0u020) +0.31 (00udu)	71 565	0.33	0.0000	0.0000	0.0000
36 ^{2}A	0.62 (u0020) +0.61 (u0002)	79 968	17.33	0.0000	0.0000	0.0019
37 ^{2}A	−0.73 (00u20) −0.43 (00u02)	81 739	6.41	0.0000	0.0002	0.0000
38 ^{2}A	−0.74 (0u002) −0.43 (0u020)	81 760	6.37	0.0002	0.0000	0.0000
39 ^{2}A	−0.97 (0002u)	98 523	0.90	0.0000	0.0000	0.0000
40 ^{2}A	0.97 (000u2)	98 559	0.89	0.0000	0.0000	0.0000

[a] 2, 0, u, and d stand for the doubly occupied, unoccupied, spin up (α), and spin down (β), respectively. [b] Spin–orbit coupling constants. [c] Contributions to the $\mathbf{D}^{SO}$ principal values.

4. Spin configuration-based analysis of the $\mathbf{D}^{SO}$(NOB-PK) tensors

In the present study, we adopted the orbital region partitioning technique (ORPT) for the analysis of the $\mathbf{D}^{SO}$(NOB-PK) tensors. As discussed in the text, the ORPT-based decomposition of the $\mathbf{D}^{SO}$ tensor allows us to discuss relationships between excited configurations and $\mathbf{D}^{SO}$ tensors, in a similar way to the ab initio methods utilising the sum-over-states equation like the hybrid CASSCF/MRMP2 method.

Traditionally, analyses of the DFT-based $\mathbf{D}^{SO}$ tensors have been carried out by means of the spin configuration basis. Namely, theoretical $\mathbf{D}^{SO}$ tensors are decomposed into four types of spin configurations: ($\alpha \rightarrow \alpha$), ($\alpha \rightarrow \beta$), ($\beta \rightarrow \alpha$) and ($\beta \rightarrow \beta$). However, the $\mathbf{D}^{SO}$ tensor analysis based on the spin configurations is not always useful, because a large amount of the $\mathbf{D}^{SO}$ contributions is cancelled out among different spin configurations. For example, let us think about the $\mathbf{D}^{SO}$ contributions from the (SOMO → unoccupied orbital) excitations. Because SOMO is occupied by a spin-α electron, the (SOMO → unoccupied orbital) excitations contribute to ($\alpha \rightarrow \alpha$) and ($\alpha \rightarrow \beta$) terms in the spin configuration-based $\mathbf{D}^{SO}$ tensor decomposition. However, if the unoccupied orbital has the same spatial distributions and orbital energies between spin-α and β, the $\mathbf{D}^{SO}(\alpha \rightarrow \alpha)$ and $\mathbf{D}^{SO}(\alpha \rightarrow \beta)$ have the same absolute value with different sign, and therefore the $\mathbf{D}^{SO}$ contributions from such (SOMO → unoccupied orbital) excitations are completely cancelled out, although both the $\mathbf{D}^{SO}(\alpha \rightarrow \alpha)$ and the $\mathbf{D}^{SO}(\alpha \rightarrow \beta)$ are nonzero. Similar cancellations also occur in the (DOR → UOR) and (DOR → SOR) excitations. Detailed discussions of the spin configuration and ORPT-based $\mathbf{D}^{SO}$ decompositions are also given in Refs. S1 and S2.

The decomposed D^{SO}(NOB-PK) contributions of the M(acac)$_3$ complexes based on the spin configurations are given in Table S6.

Table S6 Decomposed D^{SO}(NOB-PK) contributions based on spin configurations

Molecule	D^{SO}(NOB-PK)			
	$\alpha \rightarrow \alpha$	$\alpha \rightarrow \beta$	$\beta \rightarrow \alpha$	$\beta \rightarrow \beta$
V(acac)$_3$	1.8093	0.3961	−0.1281	0.1391
Cr(acac)$_3$	−0.1207	−0.2520	−0.0043	−0.0012
Mn(acac)$_3$	−0.6234	−1.6281	0.0448	−0.0734
Fe(acac)$_3$	−0.1154	0.0106	0.1320	−0.1301
Mo(acac)$_3$	−2.2283	−3.8768	1.3936	−1.3738

As discussed in Table 7 and in the text, the ORPT-based analysis revealed that a large amount of the D^{SO} contributions arises from the (SOR → SOR) excitations. The (SOR → SOR) excitations contribute to the ($\alpha \rightarrow \beta$) term in the spin configuration-based decomposition. By contrast, from Table S6, the ($\alpha \rightarrow \beta$) term is not always the largest component. The most significant case is Fe(acac)$_3$, where the D^{SO} contribution from the ($\alpha \rightarrow \beta$) spin configuration is the smallest, although all the valence d → d excitations are attributed to the ($\alpha \rightarrow \beta$) transition. In the spin configuration-based analysis, the ($\beta \rightarrow \alpha$) excitations have the largest contributions to the D^{SO} value, which

contradicts Chemist's intuition. Looking into more details, except in $Cr(acac)_3$, the D^{SO} contributions from the ($\beta \rightarrow \alpha$) and ($\beta \rightarrow \beta$) spin configurations are similar in magnitude but different in the absolute sign, and therefore most of the D^{SO} contributions from the ($\beta \rightarrow \alpha$) and ($\beta \rightarrow \beta$) excitations are cancelled out. This result is consistent with the fact that the (DOR → SOR) and (DOR → UOR) excitations are less important for the D^{SO} value. In conclusion, we highly recommend to use the ORPT-based $\mathbf{D}^{SO}$ tensor decomposition for the analysis of the DFT-based $\mathbf{D}^{SO}$ tensor calculations, instead of the traditional spin configuration-based decomposition.

References in the ESI

[S1] K. Sugisaki, K. Toyota, K. Sato, D. Shiomi, M. Kitagawa and T. Takui, An ab initio MO study of heavy atom effects on the zero-field splitting tensors of high-spin nitrenes: How the spin–orbit contributions are affected. *Phys. Chem. Chem. Phys.,* 2014, **16**, 9171–9181.

[S2] K. Sugisaki, K. Toyota, K. Sato, D. Shiomi and T. Takui, Quasi-restricted orbital treatment for the density functional theory calculations of the spin–orbit term of zero-field splitting tensors. *J. Phys. Chem. A,* 2016, **120**, 9857–9866.