

Supporting Information

Mechanistic Insights into Selective Hydrogenation of C=C Bonds Catalyzed by CCC Cobalt Pincer Complexes: A DFT Study

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1. Evaluation of density functionals

In order to evaluate the dependence of density functionals of this cobalt catalytic system, we calculated the relative free energies between key intermediates and transition states using other widely-used and/or recently developed density functionals, including B3LYP [1,2], B3LYP-D3 [3], B3PW91 [4,5], B3PW91-D3 [4-6], HSE06 [7,8], HSE06-D3 [6-8], M06 [9], M06-L [9], PBEh1PBE [10], PBEh1PBE-D3 [6,10], TPSSh [11,12], TPSSh-D3 [6,11,12] and ω B97X [13] with the same basis sets introduced above. The calculation results are listed in Table S1-S3. We can see that some functionals without dispersion corrections, such as B3LYP, B3PW91, HSE06, PBEh1PBE and TPSS, lead to obviously smaller relative free energies. The difference of relative free energies obtained by using the B3LYP-D3, B3PW91-D3, HSE06-D3, M06, M06-L, PBEh1PBE-D3, TPSSh-D3, and ω B97X-D functionals is less than 2.1 kcal/mol, which indicates a rather weak functional dependency of this system. The results of ω B97X-D are in the middle for all three reactions and very close to the results of B3LYP-D3, B3PW91-D3, M06, M06-L, TPSSh-D3 functionals. Therefore, we believe ω B97X-D is a suitable functional for the DFT study of this cobalt system.

Table S1. Absolute and relative free energies of $^s\mathbf{8}$ and $^s\mathbf{TS}_{8,4'}$ with different functionals of hydrogenation of hex-5-en-2-one.

Functionals	Absolute free energies (Hartree)		Relative energies (kcal/mol)
	$^s\mathbf{8}$	$^s\mathbf{TS}_{8,4'}$	$^s\mathbf{8} \rightarrow ^s\mathbf{TS}_{8,4'}$
B3LYP	-2145.12192049	-2145.11231285	6.0
B3LYP-D3	-2145.26562178	-2145.24783888	11.1
B3PW91	-2144.42068142	-2144.41014348	6.6
B3PW91-D3	-2144.58281460	-2144.56647261	10.3
HSE06	-2142.89797003	-2142.88521969	8.0
HSE06-D3	-2142.89797003	-2142.88300134	9.4
M06	-2143.63545911	-2143.61716095	11.5
M06-L	-2144.97800819	-2144.96133583	10.5

PBEh1PBE	-2142.94332009	-2142.93051718	8.0
PBEh1PBE-D3	-2142.94332009	-2142.92836591	9.4
TPSSh	-2145.24564335	-2145.23361687	7.5
TPSSh-D3	-2145.24564335	-2145.22833519	10.9
ω B97X	-2144.61792893	-2144.60096945	10.6
ω B97X-D	-2144.51957947	-2144.50204077	11.0

Table S2. Absolute and relative free energies of $^s\mathbf{15}$ and $^s\mathbf{TS}_{15,4'}$ with different functionals of hydrogenation of isoprene.

Functionals	Absolute free energies (Hartree)		Relative energies (kcal/mol)
	$^s\mathbf{15}$	$^s\mathbf{TS}_{15,4'}$	$^s\mathbf{15} \rightarrow ^s\mathbf{TS}_{15,4'}$
B3LYP	-2030.56026345	-2030.54976411	6.6
B3LYP-D3	-2030.70137896	-2030.68047861	13.1
B3PW91	-2029.90026749	-2029.88708003	8.3
B3PW91-D3	-2030.05952410	-2030.03970145	12.4
HSE06	-2028.44880523	-2028.43316605	9.8
HSE06-D3	-2028.44880523	-2028.43135952	11.0
M06	-2029.13574991	-2029.11453152	13.3
M06-L	-2030.42792491	-2030.40767826	12.7
PBEh1PBE	-2028.49219451	-2028.47646129	9.9
PBEh1PBE-D3	-2028.49219451	-2028.47475508	11.0
TPSSh	-2030.68124174	-2030.66640636	9.3
TPSSh-D3	-2030.68124174	-2030.66172562	12.2
ω B97X	-2030.07932278	-2030.05992191	12.2
ω B97X-D	-2029.99013866	-2029.96975901	12.8

Table S3. Absolute and relative free energies of $^s\mathbf{22}$ and $^s\mathbf{TS}_{22,4'}$ with different functionals of hydrogenation of 4-vinylcyclohex-1-ene.

Functionals	Absolute free energies (Hartree)		Relative energies (kcal/mol)
	$^s\mathbf{22}$	$^s\mathbf{TS}_{22,4'}$	$^s\mathbf{22} \rightarrow ^s\mathbf{TS}_{22,4'}$
B3LYP	-2147.28866165	-2147.28151331	4.5
B3LYP-D3	-2147.44455084	-2147.42717952	11.0
B3PW91	-2146.59118682	-2146.58266387	5.3
B3PW91-D3	-2146.76716474	-2146.75239374	9.3
HSE06	-2145.05496322	-2145.04345610	7.2
HSE06-D3	-2145.05496322	-2145.03796972	10.7

M06	-2145.77815858	-2145.76008594	11.3
M06-L	-2147.14855017	-2147.13360305	9.4
PBEh1PBE	-2145.10168895	-2145.09006144	7.3
PBEh1PBE-D3	-2145.10168895	-2145.08468371	10.7
TPSSh	-2147.42423760	-2147.41361627	6.7
TPSSh-D3	-2147.42423760	-2147.40473287	12.2
ω B97X	-2146.79137754	-2146.77268001	11.7
ω B97X-D	-2146.69862528	-2146.68151737	10.7

2. Evaluation of spin states

In order to find out correct spin-states in those reactions, we optimized the structures of triplet states of key intermediates and transition states using the same methods described above. As shown in Table S4, all triplet states are less stable than the corresponding singlet state. Therefore, we believe those cobalt catalyzed reactions goes through low-spin pathways without spin crossover.

Table S4. Absolute and relative free energies of singlet and triplet states of key intermediates and transition states.

Complexes	Absolute free energies (Hartree)		Relative energies (kcal/mol)
	Singlet	Triplet	Singlet $\rightarrow$ Triplet
3	-2868.809671	-2868.795752	8.7
4	-1832.940195	-1832.933570	4.2
4'	-1832.926881	-1832.916182	6.7
7	-2142.626976	-2142.578770	30.2
TS_{8,4'}	-2143.776614	-2143.725975	31.8
TS_{11,4'}	-2143.737038	-2143.691095	28.8
TS_{15,4'}	-2029.273656	-2029.225791	30.0
TS_{15',4}	-2029.259030	-2029.249097	6.2
TS_{19,4'}	-2029.268348	-2029.216532	32.5
21	-2144.778432	-2144.732000	29.1
TS_{22,4'}	-2145.920105	-2145.868353	32.5
22'	-2145.917494	-2145.900879	10.4
TS_{26,4'}	-2145.906571	-2145.858297	30.3
TS_{26,26'}	-2145.899038	-2145.858386	25.5
26'	-2145.897102	-2145.887213	6.2

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