Electronic Supplementary Material (ESI) for Inorganic Chemistry Frontiers.

Electronic Supplementary Information

Molecular modification of planar four-coordinated cobalt active site for electrochemical reduction of carbon dioxide. A density functional theory study

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Caption of Content

Computational Details

All quantum chemical calculations were performed with Gaussian 09 program[S1] using the *ω*B97XD[S2] density functional for all mononuclear divalent cobalt complexes. The geometry optimization and frequency calculation were operated with a mixed basis (6-311G (d, p) [S3] for C, H, O, N, S and SDD basis set[S4] for Co). The dispersion correction has been considered by using D3BJ[S5] and the natural population analysis (NPA) charge was presented. The solvent effect of water media was taken into account *via* the self-consistent reaction field (SCRF) method, using the SMD solvent model.[S6] The spin multiplicity of all structures was considered in the calculation process. The ground state of each structure was confirmed through selecting the lowest energy in these different spin number, which can greatly improve the accuracy and reliability. DOS, molecule size and d-band center were analyzed by the Multiwfn package.[S7]

The electrocatalytic mechanisms were studied based on Nøskov's computational hydrogen electrode model. This model provides an efficient approach to study proton-electron transfer in electrocatalysis without treating solvent protons explicitly and is widely used in theoretical study of electrocatalysis.[S8] In this technique, zero voltage was defined based on the potential energy (μ) of components involved in the reversible hydrogen electrode at all pH, T and p, therefore, $\mu(H^+) + \mu(e^-) = \frac{1}{2}\mu(H_2)$ at a potential of 0 V. The pathways adopted for CO_2 reduction to CO, CH_3OH and CH_4 in this work are listed Fig. 3a. The formation energies are calculated by the equation $E_{formation} = E_{Co@SUB} - E_{SUB} - E_{Co}^{2+}$, where E_{Co}^{2+} is the Gibbs Free Energy of Co^{2+}; $E_{Co@SUB}$ and E_{SUB} are the Gibbs Free Energies of SACs and substrates, respectively. For Co-porphyrin, the substrate without metal atom was saturated with H atoms on the two N atoms, thus the formation energy is defined as $E_{formation} = E_{Co@por} + 2E_H - E_{por} - E_{Co}^{2+}$, where E_H is the chemical potential of H atom.

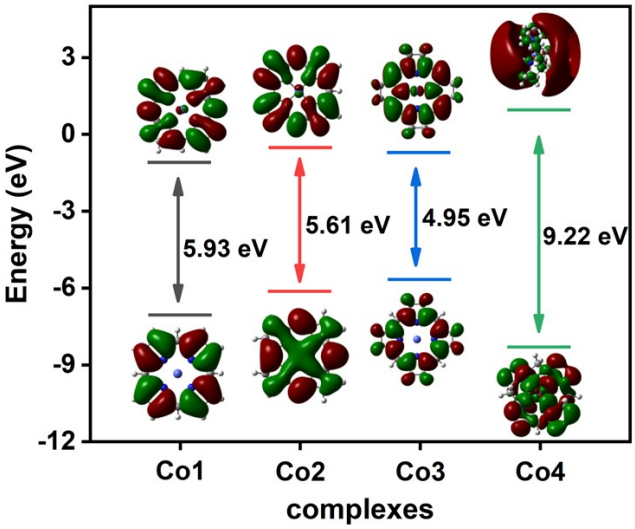

Fig. S1. The energy level of HOMO and LUMO of Co1-Co4.

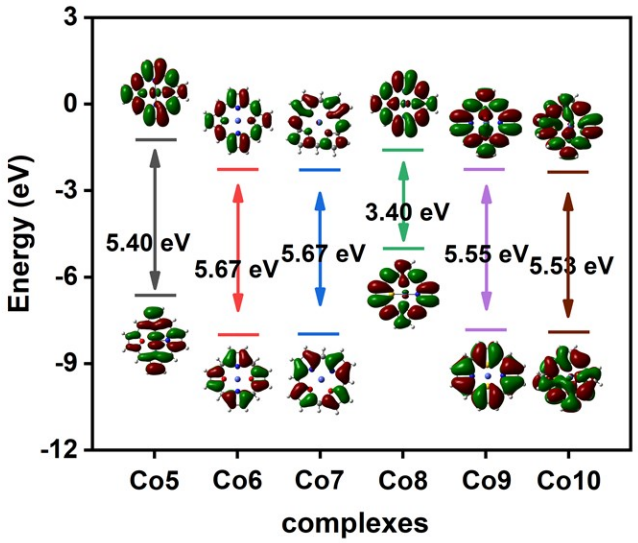

Fig. S2. The energy level of HOMO and LUMO of Co5-Co10.

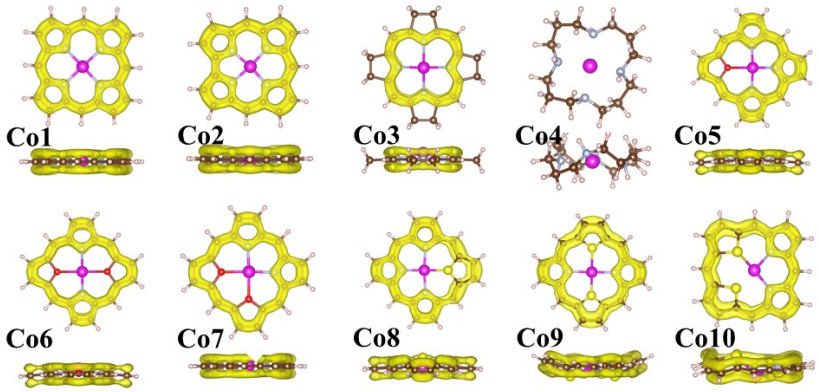

Fig. S3. LOL-π (localized orbital locator) isosurface of cobalt complexes with isovalue of 0.4.

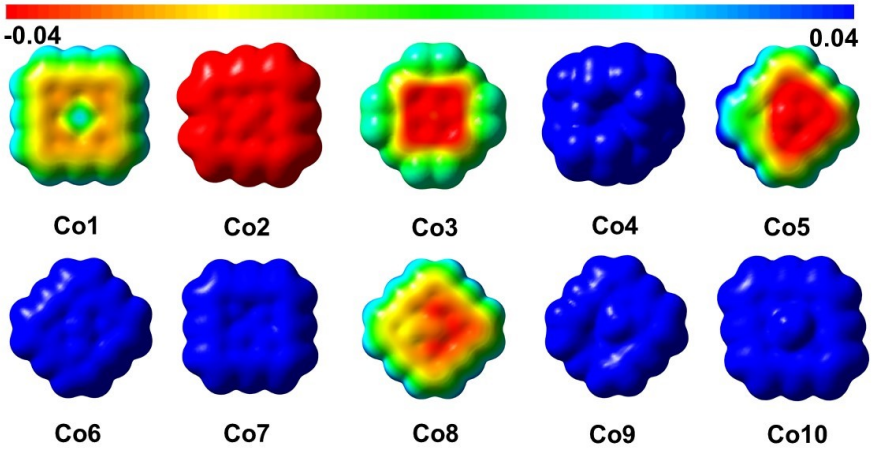

Fig. S4. Electrostatic potential (ESP) mapping on the surface of molecular electron density: Co1-Co10.

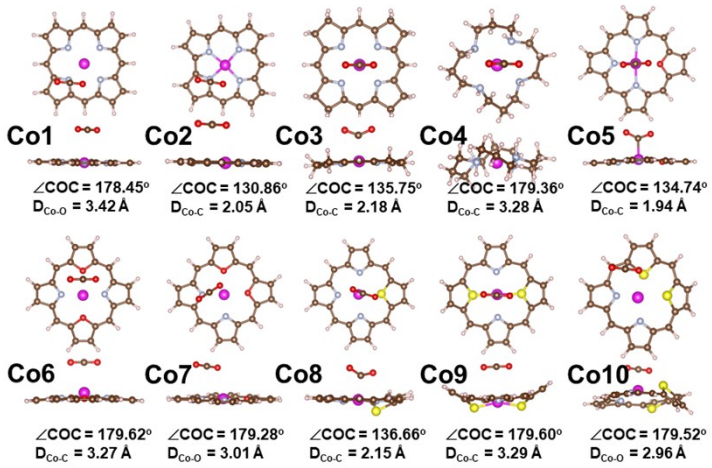

Fig. S5. Optimized structures of CO_2 adsorption on cobalt complexes. The $D_{Co-C/O}$ is the shortest distance between C or O atom in CO_2 molecule and cobalt atom.

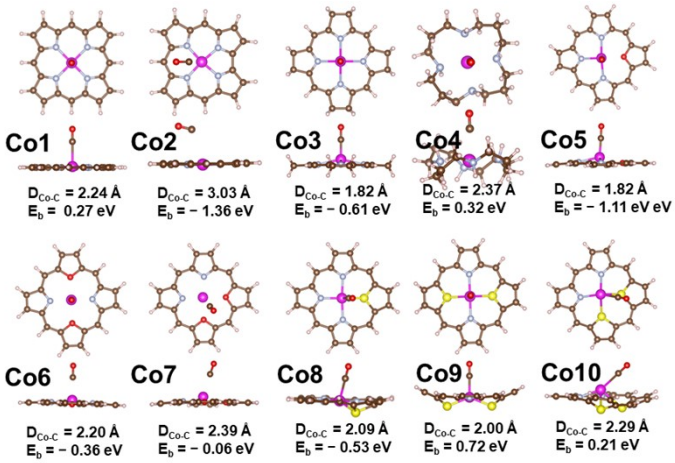

Fig. S6. Optimized structures of CO adsorption on cobalt complexes. The D_{Co-C} is the distance between C atom in CO molecule and cobalt atom. The E_b means binding energy of CO at cobalt atom.

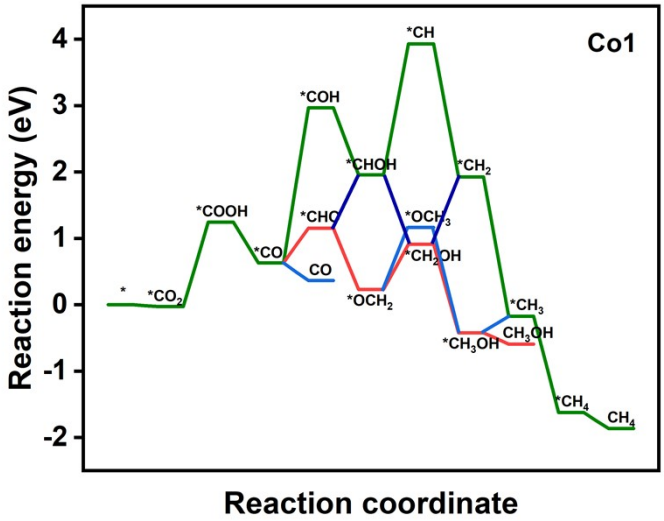

Fig. S7. The CO_2RR reaction mechanism towards CO, CH_3OH and CH_4 on Co1. The most favorable pathway towards CO product: * → *CO_2 → *COOH (PDS: 1.27 eV) → *CO → CO. The most favorable pathway towards CH_3OH product: * → *CO_2 → *COOH → *CO → *CHO → *CHOH (PDS: 0.803 eV) → *CH_2OH→ *CH_3OH→ CH_3OH. The most favorable pathway towards CH_4 product: * → *CO_2 → *COOH → *CO → *CHO → *CHOH (PDS: 0.803 eV) → *CH_2OH→ *CH_3OH → *CH_3 → *CH_4→ CH_4.

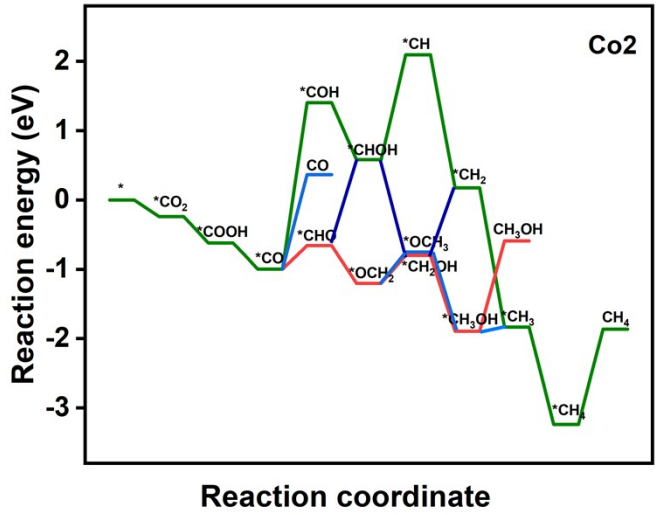

Fig. S8. The CO_2RR reaction mechanism towards CO, CH_3OH and CH_4 on Co2. The most favorable pathway towards CO product: * → *CO_2 → *COOH→ *CO → CO (PDS: 1.36 eV). The most favorable pathway towards CH_3OH product: * → *CO_2 → *COOH → *CO → *CHO → *OCH_2 → *CH_2OH→ *CH_3OH→ CH_3OH (PDS: 1.30 eV). The most favorable pathway towards CH_4 product: * → *CO_2 → *COOH → *CO → *CHO → *OCH_2 → *CH_2OH→ *CH_3OH → *CH_3 → *CH_4→ CH_4 (PDS: 1.37 eV).

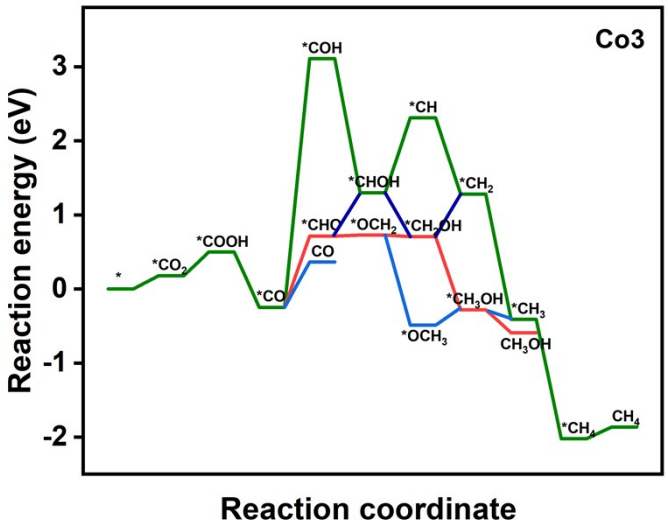

Fig. S9. The CO_2RR reaction mechanism towards CO, CH_3OH and CH_4 on Co3. The most favorable pathway towards CO product: * → *CO_2 → *COOH → *CO → CO (PDS: 0.61 eV). The most favorable pathway towards CH_3OH product: * → *CO_2 → *COOH → *CO → *CHO (PDS: 0.96 eV) → *OCH_2 → *CH_2OH→ *CH_3OH→ CH_3OH. The most favorable pathway towards CH_4 product: * → *CO_2 → *COOH → *CO → *CHO (PDS: 0.96 eV) → *OCH_2 → *CH_2OH→ *CH_3OH → *CH_3 → *CH_4→ CH_4.

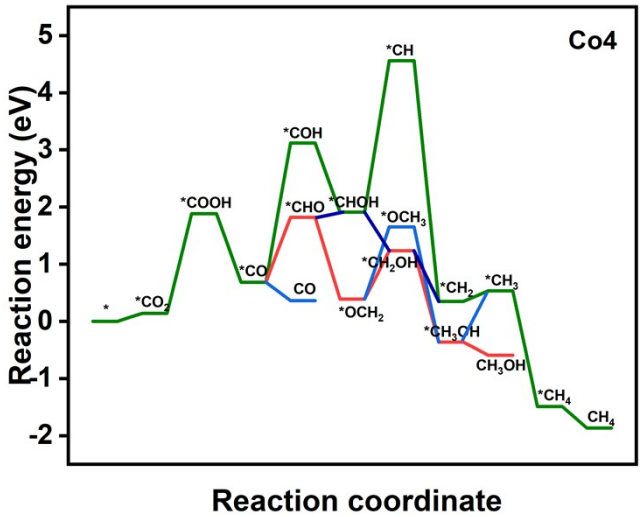

Fig. S10. The CO_2RR reaction mechanism towards CO, CH_3OH and CH_4 on Co4. The most favorable pathway towards CO product: * → *CO_2 → *COOH (PDS: 1.74 eV) → *CO → CO. The most favorable pathway towards CH_3OH product: * → *CO_2 → *COOH → *CO → *CHO (PDS: 1.14 eV) → *CHOH → *CH_2OH→ *CH_3OH→ CH_3OH. The most favorable pathway towards CH_4 product: * → *CO_2 → *COOH → *CO → *CHO (PDS: 1.14 eV) → *CHOH → *CH_2OH→ *CH_2→ *CH_3 → *CH_4→ CH_4.

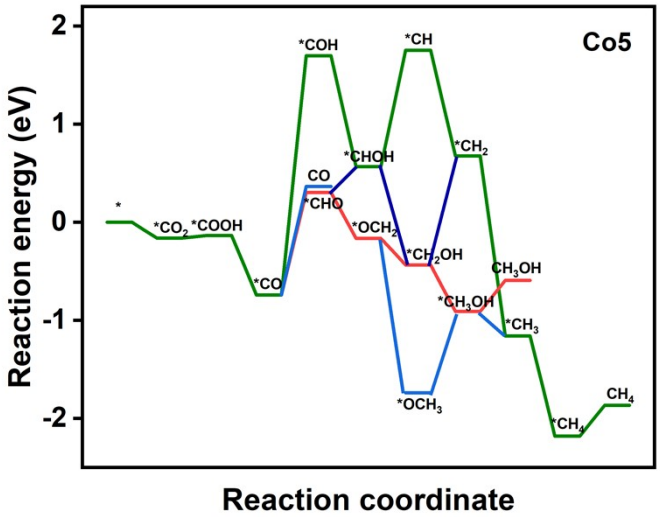

Fig. S11. The CO_2RR reaction mechanism towards CO, CH_3OH and CH_4 on Co5. The most favorable pathway towards CO product: * → *CO_2 → *COOH → *CO → CO (PDS: 1.11 eV). The most favorable pathway towards CH_3OH product: * → *CO_2 → *COOH → *CO → *CHO (PDS: 1.04 eV) → *OCH_2 → *CH_2OH→ *CH_3OH→ CH_3OH. The most favorable pathway towards CH_4 product: * → *CO_2 → *COOH → *CO → *CHO (PDS: 1.04 eV) → *OCH_2 → *CH_2OH→ *CH_3OH→ *CH_3 → *CH_4→ CH_4.

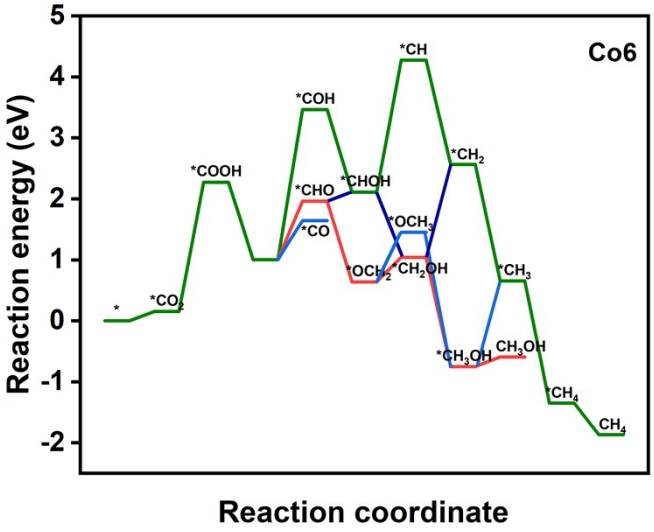

Fig. S12. The CO_2RR reaction mechanism towards CO, CH_3OH and CH_4 on Co6. The most favorable pathway towards CO product: * → *CO_2 → *COOH (PDS: 2.11 eV) → *CO → CO. The most favorable pathway towards CH_3OH product: * → *CO_2 → *COOH → *CO → *CHO (PDS: 0.96 eV) → *CHOH → *OCH_3→ *CH_3OH→ CH_3OH. The most favorable pathway towards CH_4 product: * → *CO_2 → *COOH → *CO → *CHO → *CHOH → *CH_2OH→ *CH_3OH→ *CH_3 (PDS: 1.40 eV) → *CH_4→ CH_4.

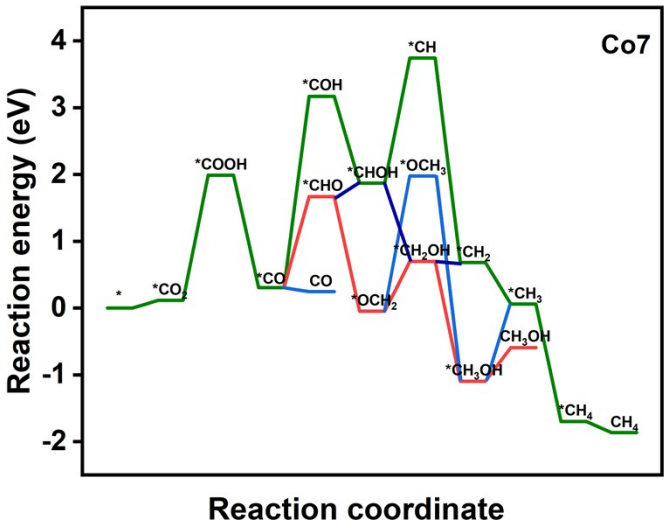

Fig. S13. The CO_2RR reaction mechanism towards CO, CH_3OH and CH_4 on Co7. The most favorable pathway towards CO product: * → *CO_2 → *COOH (PDS: 1.87 eV) → *CO → CO. The most favorable pathway towards CH_3OH product: * → *CO_2 → *COOH → *CO → *CHO (PDS: 1.36 eV) → *OCH_2 → *CH_2OH→ *CH_3OH→ CH_3OH. The most favorable pathway towards CH_4 product: * → *CO_2 → *COOH → *CO → *CHO (PDS: 1.36 eV) → *OCH_2 → *CH_2OH→ *CH_2→ *CH_3 → *CH_4→ CH_4.

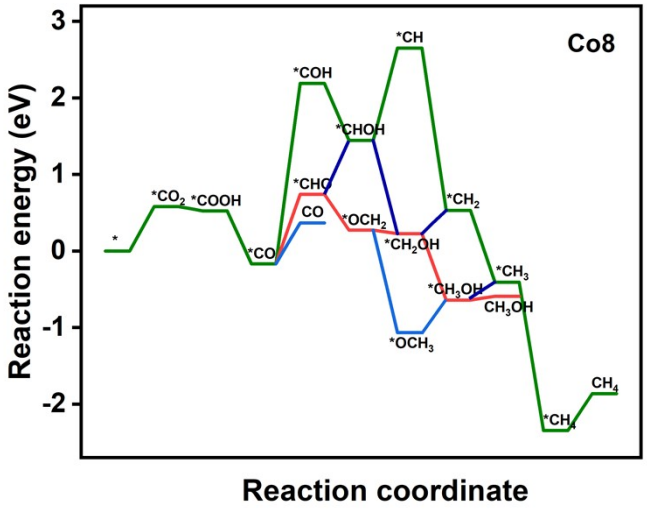

Fig. S14. The CO_2RR reaction mechanism towards CO, CH_3OH and CH_4 on Co8. The most favorable pathway towards CO product: * → *CO_2 (PDS: 0.58 eV) → *COOH → *CO → CO. The most favorable pathway towards CH_3OH product: * → *CO_2 → *COOH → *CO → *CHO (PDS: 0.91 eV) → *OCH_2 → *CH_2OH→ *CH_3OH→ CH_3OH. The most favorable pathway towards CH_4 product: * → *CO_2 → *COOH → *CO → *CHO (PDS: 0.91 eV) → *OCH_2 → *CH_2OH→ *CH_3OH→ *CH_3 → *CH_4→ CH_4.

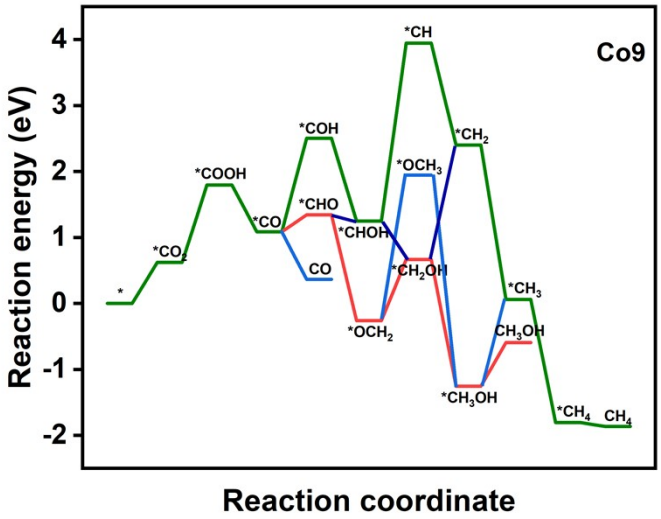

Fig. S15. The CO_2RR reaction mechanism towards CO, CH_3OH and CH_4 on Co9. The most favorable pathway towards CO product: * → *CO_2 → *COOH (PDS: 1.17 eV) → *CO → CO. The most favorable pathway towards CH_3OH product: * → *CO_2 → *COOH → *CO → *CHO → *CHOH → *CH_2OH→ *CH_3OH→ CH_3OH (PDS: 0.66 eV). The most favorable pathway towards CH_4 product: * → *CO_2 → *COOH → *CO → *CHO → *CHOH → *CH_2OH→ *CH_3OH→ *CH_3 (PDS: 1.31 eV) → *CH_4→ CH_4.

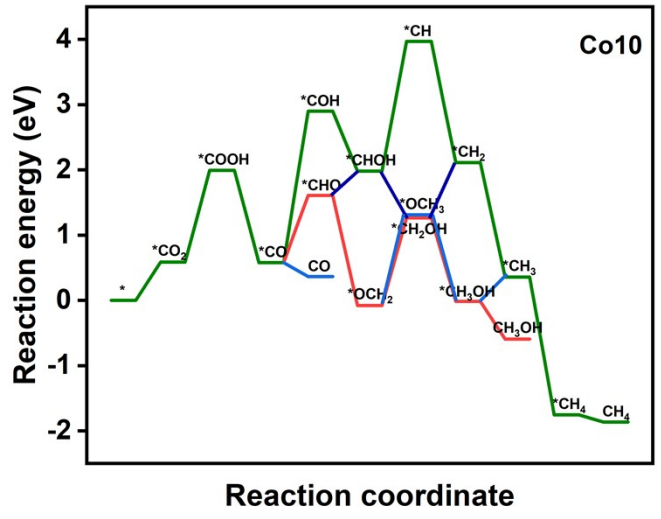

Fig. S16. The CO_2RR reaction mechanism towards CO, CH_3OH and CH_4 on Co10. The most favorable pathway towards CO product: * → *CO_2 → *COOH (PDS: 1.41 eV) → *CO → CO. The most favorable pathway towards CH_3OH product: * → *CO_2 → *COOH → *CO → *CHO (PDS: 1.03 eV) → *CHOH → *CH_2OH→ *CH_3OH→ CH_3OH. The most favorable pathway towards CH_4 product: * → *CO_2 → *COOH → *CO → *CHO (PDS: 1.03 eV) → *CHOH → *CH_2OH→ *CH_3OH→ *CH_3 → *CH_4→ CH_4.

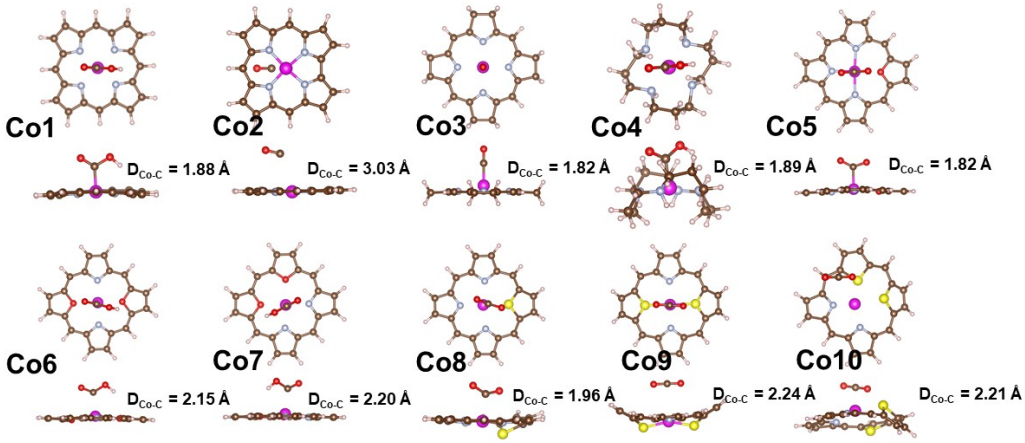

Fig. S17. Optimized structure of intermediates in potential-determining step of CO product.

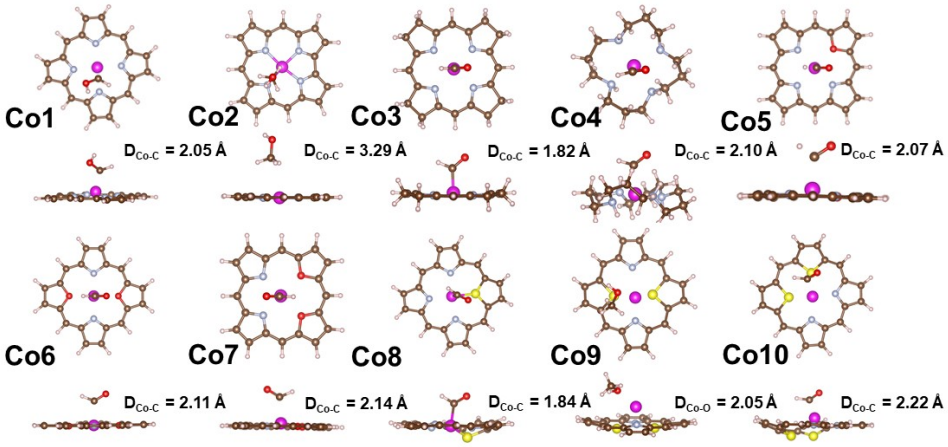

Fig. S18. Optimized structure of intermediates in potential-determining step of CH_3OH product.

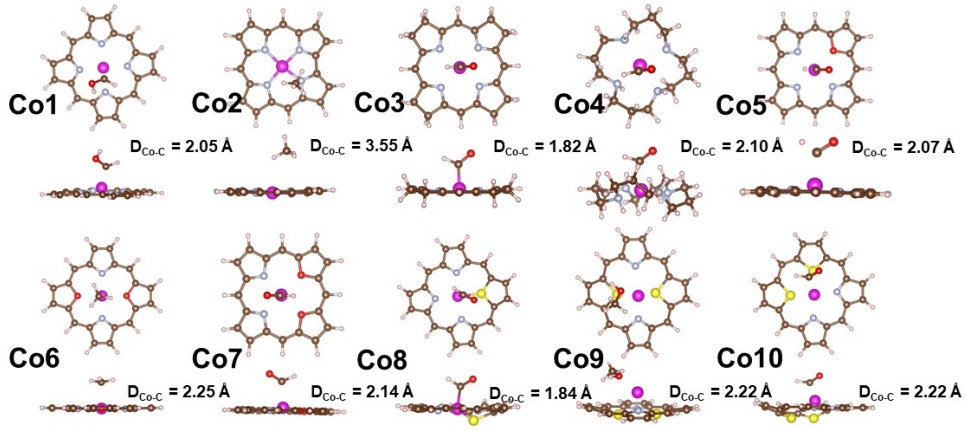

Fig. S19. Optimized structure of intermediates in potential-determining step of CH_4 product.

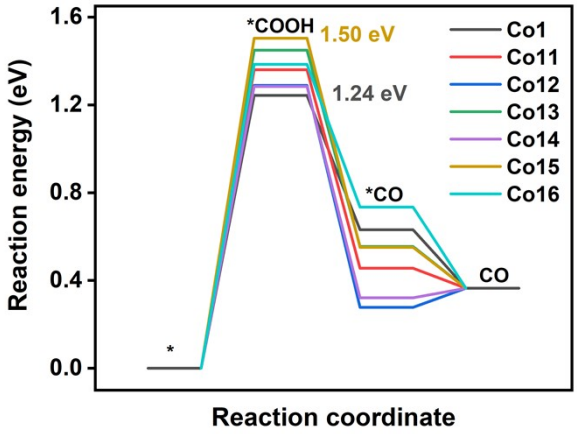

Fig. S20. Free energy diagrams of CO_2RR to CO and corresponding intermediates on Co1 and Co11-Co16 complexes. The values in figures refer to the free energy change for the potential determining step on Co1 and Co15. The asterisks mean intermediates bind at active site.

Table S1. The distance of Co-X (X =N, O, S) bond lengths on cobalt complexes.

Complexes	Co1	Co2	Co3	Co4	Co5	Co6	Co7	Co8	Co9	Co10
D_{Co-N1}	2.053	1.876	2.097	2.174	1.945	2.020	2.005	2.022	2.732	2.040
D_{Co-N2}	2.053	1.876	2.097	2.191	1.937	2.022	1.992	1.890	2.732	2.076
D_{Co-N3}	2.053	1.882	2.097	2.166	1.945			2.022		
D_{Co-N4}	2.053	1.882	2.097	2.155						
D_{Co-O1}					2.151	2.216	2.181			
D_{Co-O2}						2.215	2.158			
D_{Co-S1}								2.119	2.513	3.263
D_{Co-S2}									2.513	2.765

Table S2. The formation energy of cobalt complexes.

Complexes	Co1	Co2	Co3	Co4	Co5	Co6	Co7	Co8	Co9	Co10
Formation energy (eV)	-8.91	-11.2	-8.80	-1.88	-7.51	-1.95	-1.78	-7.50	-5.74	-0.44

Table S3. The natural population analysis of cobalt atom in cobalt complexes.

Complexes	Co1	Co2	Co3	Co4	Co5	Co6	Co7	Co8	Co9	Co10
charge	1.240	0.599	0.502	1.424	0.423	1.530	1.507	0.545	1.757	1.750

Complexes	Co11	Co12	Co13	Co14	Co15	Co16
charge	1.247	1.272	1.258	1.226	0.950	1.225

Table S4. The natural population analysis of Co, C and O atom in CO molecule, cobalt complexes and *CO intermediate. The charge difference of Co atom (ΔN_{Co}), C atom (ΔN_C) and O atom (ΔN_O) in *CO intermediate before and after CO molecule anchored into cobalt complexes.

	Co	C	O	ΔN_{Co}	ΔN_C	ΔN_O
CO		0.474	-0.474			
Co1	0.763					
Co1-CO	0.656	0.325	-0.120	-0.107	-0.149	0.354
Co2	0.714					
Co2-CO	0.701	0.136	-0.120	-0.013	-0.338	0.354
Co3	0.388					
Co3-CO	0.253	0.299	-0.258	-0.135	-0.175	0.216
Co4	1.085					
Co4-CO	-0893	0.292	-0.09	-0.192	-0.182	0.384
Co5	0.712					
Co5-CO	0.308	0.315	-0.244	-0.404	-0.159	0.230
Co6	1.516					
Co6-CO	1.145	0.636	-0.391	-0.371	0.162	0.008
Co7	1.559					
Co7-CO	1.244	0.608	-0.401	-0.315	0.134	0.073
Co8	0.709					
Co8-CO	0.319	0.406	-0.123	-0.390	-0.068	0.351
Co9	0.546					
Co9-CO	-0.003	0.52	-0.099	-0.549	0.046	0.375
Co10	1.084					
Co10-CO	0.799	0.296	-0.066	-0.285	-0.178	0.408

CO means isolated carbon monoxide molecules; Co1 represent Co1 complex; Co1-CO means *CO intermediate（CO adsorbed on Co1）.

Table S5. The energy (eV) comparison of CO desorption, *COH and *CHO intermediates generation on Co complexes.

Complexes	Co1	Co2	Co3	Co4	Co5	Co6	Co7	Co8	Co9	Co10
ΔE_{CO}	-0.27	1.36	0.61	-0.32	1.11	0.64	-0.06	0.53	-0.72	-0.21
ΔE_{COH}	2.34	2.40	3.36	2.43	2.44	2.46	3.17	2.35	1.41	2.32
ΔE_{CHO}	0.52	0.34	0.96	1.14	1.04	0.96	1.67	0.91	0.25	1.03

Table S6. Proposed elementary steps and free energy changes for CO_2RR pathways on Co complexes.

Elementary step	ΔG/eV			
	Co1	Co2	Co3	Co4
$* + CO_2 \rightarrow *CO_2$	-0.03	-0.24	-0.17	0.14
$*CO_2 + H^+ + e^- \rightarrow *COOH$	1.27	-0.38	0.32	1.74
$*COOH + H^+ + e^- \rightarrow *CO + H_2O$	-0.61	-0.38	-0.75	-1.20
$*CO \rightarrow * + CO$	-0.27	1.36	0.61	-0.32
$*CO + H^+ + e^- \rightarrow *COH$	2.34	2.40	3.36	2.43
$*CO + H^+ + e^- \rightarrow *CHO$	0.52	0.34	0.96	1.14
$*COH + H^+ + e^- \rightarrow *CHOH$	-1.02	-0.82	-1.81	-1.21
$*CHO + H^+ + e^- \rightarrow *CHOH$	0.80	1.24	0.58	0.09
$*CHO + H^+ + e^- \rightarrow *OCH_2$	-0.92	-0.54	0.01	-1.43
$*CHOH + H^+ + e^- \rightarrow *CH + H_2O$	1.97	1.51	1.01	2.65
$*CHOH + H^+ + e^- \rightarrow *CH_2OH$	-1.04	-1.38	-0.59	-0.67
$*OCH_2 + H^+ + e^- \rightarrow *CH_2OH$	0.68	0.40	-0.02	0.85
$*OCH_2 + H^+ + e^- \rightarrow *OCH_3$	0.94	0.45	-1.21	1.26
$*CH + H^+ + e^- \rightarrow *CH_2$	-2.01	-1.92	-1.03	-4.21
$*CH_2OH + H^+ + e^- \rightarrow *CH_2 + H_2O$	1.01	0.98	0.57	-0.89
$*CH_2OH + H^+ + e^- \rightarrow *CH_3OH$	-1.33	-1.09	-0.99	-1.60
$*OCH_3 + H^+ + e^- \rightarrow *CH_3OH$	-1.59	-1.14	0.21	-2.01
$*CH_2 + H^+ + e^- \rightarrow *CH_3$	-2.10	-2.01	-1.69	0.19
$*CH_3OH + H^+ + e^- \rightarrow *CH_3 + H_2O$	0.25	0.06	-0.13	0.90
$*CH_3OH \rightarrow * + CH_3OH$	-0.17	1.30	-0.31	-0.23
$*CH_3 + H^+ + e^- \rightarrow *CH_4$	-1.45	-1.40	-1.61	-2.02
$*CH_4 \rightarrow * + CH_4$	-0.24	-1.37	0.15	-0.38

Elementary step	ΔG/eV					
	Co5	Co6	Co7	Co8	Co9	Co10
$* + CO_2 \rightarrow *CO_2$	-0.16	0.15	0.11	0.58	0.62	0.59
$*CO_2 + H^+ + e^- \rightarrow *COOH$	0.03	2.12	1.88	0.06	1.17	1.41
$*COOH + H^+ + e^- \rightarrow *CO + H_2O$	-0.61	-1.27	-1.69	-0.69	-0.71	-1.42
$*CO \rightarrow * + CO$	1.11	-0.64	0.06	0.53	-0.72	0.21
$*CO + H^+ + e^- \rightarrow *COH$	2.44	2.46	2.87	2.36	1.42	2.32
$*CO + H^+ + e^- \rightarrow *CHO$	1.04	0.96	1.36	0.91	0.26	1.03
$*COH + H^+ + e^- \rightarrow *CHOH$	-1.32	-1.35	-1.30	-0.74	-1.25	-0.92
$*CHO + H^+ + e^- \rightarrow *CHOH$	0.26	0.15	0.20	0.70	-0.09	0.37
$*CHO + H^+ + e^- \rightarrow *OCH_2$	-0.46	-1.32	-1.71	-0.47	-1.60	-1.69
$*CHOH + H^+ + e^- \rightarrow *CH + H_2O$	1.19	2.16	1.87	1.21	2.69	1.98
$*CHOH + H^+ + e^- \rightarrow *CH_2OH$	-1.00	-1.07	-1.17	-1.22	-0.58	-0.72
$*OCH_2 + H^+ + e^- \rightarrow *CH_2OH$	-0.27	0.40	0.75	-0.05	0.93	1.34
$*OCH_2 + H^+ + e^- \rightarrow *OCH_3$	-1.58	0.81	2.02	-1.34	2.21	1.39
$*CH + H^+ + e^- \rightarrow *CH_2$	-1.08	-1.71	-3.06	-2.12	-1.55	-1.86
$*CH_2OH + H^+ + e^- \rightarrow *CH_2 + H_2O$	1.11	1.52	-0.01	0.30	1.73	0.84
$*CH_2OH + H^+ + e^- \rightarrow *CH_3OH$	-0.47	-1.79	-1.79	-0.87	-1.92	-1.28
$*OCH_3 + H^+ + e^- \rightarrow *CH_3OH$	0.83	-2.20	-3.07	0.42	-3.20	-1.33
$*CH_2 + H^+ + e^- \rightarrow *CH_3$	-1.83	-1.91	-0.62	-0.94	-2.34	-1.75
$*CH_3OH + H^+ + e^- \rightarrow *CH_3 + H_2O$	-0.25	1.41	1.16	0.23	1.32	0.37
$*CH_3OH \rightarrow * + CH_3OH$	0.32	0.16	0.50	0.05	0.66	-0.58
$*CH_3 + H^+ + e^- \rightarrow *CH_4$	-1.02	-2.01	-1.76	-1.94	-1.86	-2.11
$*CH_4 \rightarrow * + CH_4$	0.31	-0.52	-0.17	0.48	-0.06	-0.11

Table S7. Summary of CO_2RR potential determining steps (PDS), limiting potential (U_L) on Co1-Co10.

Catalysts	Products	PDS	ΔG/eV	U_L
Co1	CO	$*CO_2 + H^+ + e^- \rightarrow *COOH$	1.27	-1.27
	CH_3OH	$*CHO + H^+ + e^- \rightarrow *CHOH$	0.80	-0.80
	CH_4	$*CHO + H^+ + e^- \rightarrow *CHOH$	0.80	-0.80
Co2	CO	$*CO \rightarrow * + CO$	1.36	-1.36
	CH_3OH	$*CH_3OH \rightarrow * + CH_3OH$	1.30	-1.30
	CH_4	$*CH_4 \rightarrow * + CH_4$	1.37	-1.37
Co3	CO	$*CO \rightarrow * + CO$	0.61	-0.61
	CH_3OH	$*CO + H^+ + e^- \rightarrow * + CHO$	0.96	-0.96
	CH_4	$*CO + H^+ + e^- \rightarrow * + CHO$	0.96	-0.96
Co4	CO	$*CO_2 + H^+ + e^- \rightarrow *COOH$	1.74	-1.74
	CH_3OH	$*CO + H^+ + e^- \rightarrow * + CHO$	1.14	-1.14
	CH_4	$*CO + H^+ + e^- \rightarrow * + CHO$	1.14	-1.14
Co5	CO	$*CO \rightarrow * + CO$	1.11	-1.11
	CH_3OH	$*CO + H^+ + e^- \rightarrow * + CHO$	1.04	-1.04
	CH_4	$*CO + H^+ + e^- \rightarrow * + CHO$	1.04	-1.04
Co6	CO	$*CO_2 + H^+ + e^- \rightarrow *COOH$	2.11	-2.11
	CH_3OH	$*CO + H^+ + e^- \rightarrow * + CHO$	0.96	-0.96
	CH_4	$*CH_3OH + H^+ + e^- \rightarrow *CH_3 + H_2O$	1.40	-1.40
Co7	CO	$*CO_2 + H^+ + e^- \rightarrow *COOH$	1.87	-1.87
	CH_3OH	$*CO + H^+ + e^- \rightarrow * + CHO$	1.36	-1.36
	CH_4	$*CO + H^+ + e^- \rightarrow * + CHO$	1.36	-1.36
Co8	CO	$* + CO_2 \rightarrow *CO_2$	0.58	-0.58
	CH_3OH	$*CO + H^+ + e^- \rightarrow * + CHO$	0.91	-0.91
	CH_4	$*CO + H^+ + e^- \rightarrow * + CHO$	0.91	-0.91
Co9	CO	$*CO_2 + H^+ + e^- \rightarrow *COOH$	1.17	-1.17
	CH_3OH	$*CH_3OH \rightarrow * + CH_3OH$	0.66	-0.66
	CH_4	$*CH_3OH + H^+ + e^- \rightarrow *CH_3 + H_2O$	1.20	-1.20
Co10	CO	$*CO_2 + H^+ + e^- \rightarrow *COOH$	1.41	-1.41
	CH_3OH	$*CO + H^+ + e^- \rightarrow * + CHO$	1.03	-1.03
	CH_4	$*CO + H^+ + e^- \rightarrow * + CHO$	1.03	-1.03

Table S8. The cartesian coordinates of all catalysts.

Model Co1			
Co	0.00000000	0.00000000	0.00010000
N	-1.46100000	-1.44170000	-0.00010000
C	-2.80780000	-1.22670000	-0.00060000
C	-1.26400000	-2.79120000	0.00040000
C	-3.49600000	-2.49640000	-0.00070000
C	-2.54280000	-3.46240000	0.00020000
H	-4.57010000	-2.61690000	-0.00130000
H	-2.67780000	-4.53480000	0.00050000
N	1.44190000	-1.46080000	0.00020000
C	2.79140000	-1.26400000	-0.00030000
C	1.22680000	-2.80750000	0.00070000
C	3.46250000	-2.54280000	-0.00060000
C	2.49630000	-3.49590000	0.00060000
H	4.53490000	-2.67800000	-0.00130000
H	2.61670000	-4.57000000	0.00110000
N	1.46100000	1.44170000	-0.00010000
C	1.26400000	2.79120000	0.00040000
C	2.80780000	1.22670000	-0.00060000
C	2.54280000	3.46240000	0.00020000
C	3.49600000	2.49640000	-0.00070000
H	2.67780000	4.53480000	0.00050000
H	4.57010000	2.61690000	-0.00130000
N	-1.44190000	1.46080000	0.00030000
C	-1.22680000	2.80750000	0.00080000
C	-2.79140000	1.26400000	-0.00030000
C	-2.49630000	3.49590000	0.00060000
C	-3.46250000	2.54280000	-0.00060000
H	-2.61670000	4.57000000	0.00100000
H	-4.53490000	2.67790000	-0.00130000
C	3.42370000	-0.02280000	-0.00090000
C	0.02280000	3.42340000	0.00090000
C	-3.42370000	0.02280000	-0.00080000
C	-0.02280000	-3.42340000	0.00090000
H	-0.02980000	-4.50800000	0.00140000
H	-4.50840000	0.02980000	-0.00130000
H	0.02980000	4.50800000	0.00140000
H	4.50840000	-0.02980000	-0.00140000
Model Co2			
Co	-0.02230000	0.00000000	0.00000000
N	-1.27420000	-1.40550000	0.00040000
C	-2.62830000	-1.23760000	0.00000000
C	-1.00180000	-2.76440000	0.00020000
C	-3.25330000	-2.53900000	-0.00040000
C	-2.26000000	-3.46690000	-0.00030000
H	-4.32110000	-2.70800000	-0.00060000
H	-2.36010000	-4.54370000	-0.00070000
N	-1.27410000	1.40550000	0.00030000
C	-1.00160000	2.76450000	0.00020000
C	-2.62820000	1.23770000	0.00010000
C	-2.25980000	3.46700000	-0.00010000
C	-3.25320000	2.53910000	-0.00010000
H	-2.35990000	4.54380000	-0.00030000

H	-4.32100000	2.70820000	-0.00020000
N	1.40590000	1.21680000	-0.00020000
C	2.66890000	0.71510000	-0.00040000
C	1.45160000	2.57890000	0.00010000
C	3.58160000	1.79740000	-0.00030000
C	2.82410000	2.96120000	0.00010000
H	4.65980000	1.72170000	-0.00050000
H	3.19340000	3.97760000	0.00040000
N	1.40590000	-1.21680000	-0.00020000
C	2.66880000	-0.71520000	-0.00030000
C	1.45150000	-2.57900000	0.00030000
C	3.58150000	-1.79760000	0.00000000
C	2.82400000	-2.96140000	0.00020000
H	4.65970000	-1.72190000	0.00010000
H	3.19330000	-3.97770000	0.00050000
C	-3.27340000	0.00010000	0.00000000
C	0.26270000	-3.32990000	0.00030000
C	0.26280000	3.32990000	0.00020000
H	0.33070000	-4.41220000	0.00030000
H	0.33090000	4.41220000	0.00030000
H	-4.35730000	0.00010000	-0.00020000
Model Co3			
Co	0.00000000	0.00000000	0.00000000
N	-0.03220000	-2.09640000	0.00000000
C	1.06160000	-2.89140000	-0.00020000
C	-1.15030000	-2.85720000	0.00020000
C	0.69780000	-4.35970000	-0.00020000
C	-0.83210000	-4.33580000	0.00020000
H	1.11370000	-4.85710000	0.87930000
H	-1.26260000	-4.82030000	0.88000000
N	-2.09640000	0.03220000	0.00000000
C	-2.85720000	1.15030000	-0.00030000
C	-2.89140000	-1.06160000	0.00030000
C	-4.33580000	0.83210000	-0.00030000
C	-4.35970000	-0.69780000	0.00020000
H	-4.82040000	1.26320000	0.87920000
H	-4.85710000	-1.11380000	-0.87930000
N	0.03220000	2.09640000	0.00010000
C	1.15030000	2.85720000	0.00030000
C	-1.06160000	2.89140000	-0.00020000
C	0.83210000	4.33580000	0.00020000
C	-0.69780000	4.35970000	-0.00020000
H	1.26260000	4.82030000	0.88000000
H	-1.11370000	4.85710000	0.87930000
N	2.09640000	-0.03220000	0.00000000
C	2.89140000	1.06160000	0.00020000
C	2.85720000	-1.15030000	-0.00020000
C	4.35970000	0.69780000	0.00020000
C	4.33580000	-0.83210000	-0.00030000
H	4.85710000	1.11370000	-0.87940000
H	4.82040000	-1.26310000	0.87920000
C	-2.38060000	2.45520000	-0.00040000
C	2.45520000	2.38060000	0.00040000
C	2.38060000	-2.45520000	-0.00040000

C	-2.45520000	-2.38060000	0.00040000
H	-3.23460000	-3.13650000	0.00060000
H	3.13650000	-3.23460000	-0.00060000
H	3.23460000	3.13650000	0.00050000
H	-3.13650000	3.23460000	-0.00070000
H	4.82030000	-1.26260000	-0.88000000
H	4.85700000	1.11320000	0.88000000
H	1.26320000	4.82040000	-0.87920000
H	-1.11320000	4.85700000	-0.88010000
H	-4.82030000	1.26260000	-0.88010000
H	-4.85700000	-1.11320000	0.88010000
H	-1.26310000	-4.82040000	-0.87920000
H	1.11320000	-4.85700000	-0.88000000
Model Co4			
Co	0.00210000	0.00130000	-0.07300000
N	-2.18270000	-0.00700000	0.09200000
C	-2.67800000	0.94990000	-0.91880000
C	-2.76730000	-1.34260000	-0.11840000
N	-0.05240000	-2.16290000	-0.15190000
C	1.26100000	-2.82690000	-0.29410000
C	-0.80330000	-2.60660000	1.03890000
N	2.07910000	-0.18980000	0.46920000
C	2.76840000	1.03680000	0.92670000
C	2.88260000	-0.88050000	-0.57030000
N	-0.04590000	2.16950000	-0.22700000
C	1.11040000	2.88960000	0.35490000
C	-1.29240000	2.71880000	0.34740000
C	2.14450000	-2.03210000	-1.24790000
C	2.46280000	2.25700000	0.06830000
C	-2.53850000	2.40060000	-0.46640000
C	-2.31840000	-2.38150000	0.90230000
H	-2.72010000	-2.11780000	1.88450000
H	2.88860000	-2.69140000	-1.70000000
H	-2.79760000	-3.31970000	0.61150000
H	-0.61510000	-3.66890000	1.22570000
H	-0.40220000	-2.05620000	1.89460000
H	-3.86050000	-1.27370000	-0.08180000
H	-2.51280000	-1.65400000	-1.13560000
H	-2.11520000	0.77470000	-1.83990000
H	-3.73130000	0.74830000	-1.14240000
H	-2.57170000	3.03540000	-1.35610000
H	-3.39780000	2.67510000	0.15230000
H	-1.38150000	2.32100000	1.36190000
H	-1.20660000	3.80710000	0.44060000
H	1.09600000	3.92240000	-0.00990000
H	0.95520000	2.92890000	1.43710000
H	3.22530000	3.01100000	0.28170000
H	2.55660000	2.01850000	-0.99680000
H	2.45580000	1.23130000	1.95550000
H	3.84840000	0.85200000	0.94460000
H	3.17330000	-0.14080000	-1.31790000
H	3.80140000	-1.25160000	-0.10220000
H	1.51820000	-1.65710000	-2.06490000
H	1.72140000	-2.90260000	0.69530000

H	1.11360000	-3.84920000	-0.65470000
H	-0.05000000	2.37410000	-1.22520000
H	-0.58350000	-2.41650000	-0.98110000
H	-2.48020000	0.31490000	1.01130000
H	2.03760000	-0.81480000	1.26990000
Model Co5			
Co	0.00000000	0.00000000	0.07930000
N	0.00000000	0.00000000	2.01620000
C	0.00000000	1.08630000	2.84730000
C	0.00000000	-1.08630000	2.84730000
C	0.00000000	0.67790000	4.22470000
C	0.00000000	-0.67790000	4.22470000
H	0.00000000	1.35660000	5.06570000
H	0.00000000	-1.35660000	5.06570000
N	0.00000000	-1.94420000	0.02510000
C	0.00000000	-2.76780000	-1.07020000
C	0.00000000	-2.79770000	1.10430000
C	0.00000000	-4.15920000	-0.67500000
C	0.00000000	-4.17590000	0.67260000
H	0.00000000	-4.98840000	-1.36770000
H	0.00000000	-5.02470000	1.34160000
C	0.00000000	1.10790000	-2.89690000
C	0.00000000	-1.10790000	-2.89690000
C	0.00000000	0.68390000	-4.23310000
C	0.00000000	-0.68390000	-4.23310000
H	0.00000000	1.35610000	-5.07730000
H	0.00000000	-1.35610000	-5.07730000
N	0.00000000	1.94420000	0.02510000
C	0.00000000	2.76780000	-1.07020000
C	0.00000000	2.79770000	1.10430000
C	0.00000000	4.15920000	-0.67500000
C	0.00000000	4.17590000	0.67260000
H	0.00000000	4.98840000	-1.36770000
H	0.00000000	5.02470000	1.34160000
C	0.00000000	-2.38470000	-2.39800000
C	0.00000000	2.38470000	-2.39800000
C	0.00000000	2.40600000	2.42190000
C	0.00000000	-2.40600000	2.42190000
H	0.00000000	-3.18070000	3.18010000
H	0.00000000	3.18070000	3.18010000
H	0.00000000	3.17040000	-3.14390000
H	0.00000000	-3.17040000	-3.14390000
O	0.00000000	0.00000000	-2.07150000
Model Co6			
Co	-0.00190000	0.00230000	0.47080000
C	-2.97170000	1.08920000	-0.05630000
C	-2.95230000	-1.13460000	-0.02650000
C	-4.30840000	0.65030000	-0.09310000
C	-4.29650000	-0.72010000	-0.07380000
H	-5.16210000	1.30880000	-0.13680000
H	-5.13850000	-1.39440000	-0.09890000
N	0.02220000	-1.96600000	0.00720000
C	1.12000000	-2.77040000	-0.08320000

C	-1.06760000	-2.78240000	-0.05320000
C	0.70900000	-4.15000000	-0.19810000
C	-0.64330000	-4.15780000	-0.17790000
H	1.38840000	-4.98450000	-0.29020000
H	-1.31510000	-5.00020000	-0.25080000
C	2.94950000	1.13160000	-0.02900000
C	2.97120000	-1.09060000	-0.05490000
C	4.29290000	0.71930000	-0.07260000
C	4.30630000	-0.65220000	-0.09020000
H	5.13410000	1.39460000	-0.09680000
H	5.16050000	-1.31000000	-0.13130000
N	-0.01570000	1.96650000	0.00090000
C	1.07300000	2.78710000	-0.05640000
C	-1.11610000	2.76730000	-0.08570000
C	0.64420000	4.16080000	-0.17490000
C	-0.70840000	4.14830000	-0.19380000
C	2.45300000	-2.36920000	-0.08610000
C	2.41100000	2.40300000	-0.04110000
C	-2.45100000	2.36560000	-0.08790000
C	-2.40930000	-2.40180000	-0.03780000
H	-3.13780000	-3.20330000	-0.07380000
H	-3.19240000	3.15400000	-0.14310000
H	3.14360000	3.20080000	-0.07560000
H	3.19590000	-3.15620000	-0.14230000
H	1.31250000	5.00640000	-0.24370000
H	-1.39020000	4.98150000	-0.27990000
O	-2.16440000	-0.01530000	-0.00890000
O	2.16120000	0.01240000	-0.01230000
Model Co7			
Co	0.02030000	0.09230000	0.01850000
C	-1.03540000	2.88010000	-0.00430000
C	-2.70240000	1.45520000	-0.00160000
C	-2.25420000	3.65780000	-0.01490000
C	-3.28440000	2.77840000	-0.01300000
H	-2.29360000	4.73720000	-0.02480000
H	-4.34470000	2.98340000	-0.02130000
C	-1.48110000	-2.69770000	0.00110000
C	-2.96800000	-1.03400000	0.00170000
C	-2.76730000	-3.26990000	-0.00430000
C	-3.67940000	-2.24870000	-0.00250000
H	-2.95730000	-4.33190000	-0.00770000
H	-4.75590000	-2.32030000	-0.00290000
C	2.76850000	-1.46840000	-0.00370000
C	1.04860000	-2.89530000	-0.00580000
C	3.29020000	-2.77530000	-0.01350000
C	2.23650000	-3.65050000	-0.01280000
H	4.34440000	-3.00450000	-0.01600000
H	2.26750000	-4.72900000	-0.01530000
N	1.57140000	1.34200000	0.01570000
C	2.89200000	1.03580000	0.00730000
C	1.45910000	2.69710000	0.00330000
C	3.66700000	2.25610000	-0.00540000
C	2.78150000	3.28190000	-0.00880000
C	-0.25910000	-3.34740000	-0.00360000

C	3.42500000	-0.25510000	0.00270000
C	0.25730000	3.40370000	-0.00440000
C	-3.43190000	0.26420000	-0.00060000
H	-4.51180000	0.35530000	-0.00180000
H	0.33710000	4.48480000	-0.01550000
H	4.50590000	-0.33540000	-0.00160000
H	-0.34370000	-4.42820000	-0.00650000
H	4.74610000	2.30010000	-0.01300000
H	2.98390000	4.34270000	-0.01890000
O	1.39640000	-1.57000000	-0.00470000
N	-1.34970000	1.55580000	0.00460000
O	-1.62820000	-1.33490000	0.00500000
Model Co8			
Co	-0.26750000	0.00000000	-0.00010000
N	-0.07200000	2.01230000	0.00000000
C	1.03610000	2.86080000	0.00010000
C	-1.17250000	2.83300000	-0.00010000
C	0.59730000	4.20480000	0.00020000
C	-0.77760000	4.19210000	0.00000000
H	1.25770000	5.06060000	0.00030000
H	-1.45640000	5.03290000	0.00000000
N	-2.15740000	0.00000000	0.00000000
C	-2.96410000	-1.10570000	0.00020000
C	-2.96410000	1.10560000	0.00000000
C	-4.34970000	-0.67510000	0.00030000
C	-4.34970000	0.67500000	0.00010000
H	-5.19670000	-1.34630000	0.00050000
H	-5.19680000	1.34630000	0.00000000
N	-0.07190000	-2.01230000	0.00000000
C	1.03620000	-2.86080000	0.00000000
C	-1.17250000	-2.83300000	0.00010000
C	0.59740000	-4.20480000	0.00010000
C	-0.77750000	-4.19210000	0.00020000
H	1.25770000	-5.06060000	0.00010000
H	-1.45640000	-5.03290000	0.00030000
C	2.96910000	-1.29680000	-0.00020000
C	2.96900000	1.29680000	0.00010000
C	4.28100000	-0.68190000	0.00010000
C	4.28100000	0.68200000	0.00020000
H	5.18250000	-1.28040000	0.00020000
H	5.18250000	1.28050000	0.00050000
C	-2.52040000	-2.40490000	0.00020000
C	2.43880000	-2.54690000	0.00000000
C	2.43880000	2.54690000	0.00030000
C	-2.52050000	2.40490000	-0.00010000
H	-3.27230000	3.18580000	-0.00010000
H	3.10960000	3.39930000	0.00050000
H	3.10960000	-3.39930000	0.00010000
H	-3.27230000	-3.18580000	0.00040000
S	1.85160000	0.00000000	-0.00060000
Model Co9			
Co	0.00000000	0.00000000	1.40450000
C	-1.70880000	-2.51660000	-0.25960000

C	0.78650000	-2.94550000	-0.26010000
C	-1.35610000	-3.87710000	-0.11940000
C	0.00000000	-4.11030000	-0.11980000
H	-2.10620000	-4.64520000	0.01720000
H	0.45050000	-5.08470000	0.01710000
N	2.22840000	-0.38260000	-0.12860000
C	3.20900000	0.55400000	-0.12720000
C	2.84840000	-1.58860000	-0.12580000
C	4.51510000	-0.08130000	-0.09430000
C	4.29030000	-1.41620000	-0.09310000
H	5.46130000	0.44010000	-0.08550000
H	5.01360000	-2.21870000	-0.08400000
C	-0.78650000	2.94550000	-0.26010000
C	1.70880000	2.51660000	-0.25960000
C	0.00000000	4.11030000	-0.11980000
C	1.35610000	3.87710000	-0.11940000
H	-0.45050000	5.08470000	0.01710000
H	2.10620000	4.64520000	0.01720000
N	-2.22840000	0.38260000	-0.12860000
C	-2.84840000	1.58860000	-0.12580000
C	-3.20900000	-0.55400000	-0.12720000
C	-4.29030000	1.41620000	-0.09310000
C	-4.51510000	0.08130000	-0.09430000
H	-5.01360000	2.21870000	-0.08400000
H	-5.46130000	-0.44010000	-0.08550000
C	2.96340000	1.93140000	-0.15970000
C	-2.16390000	2.80890000	-0.15960000
C	-2.96340000	-1.93140000	-0.15970000
C	2.16390000	-2.80890000	-0.15960000
H	2.74570000	-3.72020000	-0.07050000
H	-3.81330000	-2.60000000	-0.07160000
H	-2.74570000	3.72020000	-0.07050000
H	3.81330000	2.60000000	-0.07160000
S	-0.26030000	-1.56850000	-0.54200000
S	0.26030000	1.56850000	-0.54200000
Model Co10			
Co	0.43010000	0.32100000	1.10090000
C	-1.37920000	-2.81690000	-0.34630000
C	1.13300000	-2.90960000	-0.01220000
C	-0.88350000	-4.09080000	0.06130000
C	0.47020000	-4.14130000	0.24540000
H	-1.55770000	-4.91140000	0.26950000
H	1.00220000	-5.00120000	0.63030000
N	2.17420000	-0.11150000	0.13500000
C	2.99660000	0.94760000	-0.15920000
C	2.93960000	-1.23380000	0.09020000
C	4.34350000	0.46550000	-0.35060000
C	4.31200000	-0.87890000	-0.17080000
H	5.18860000	1.08690000	-0.60860000
H	5.12170000	-1.58770000	-0.26120000
C	-0.90100000	2.96220000	0.00950000
C	1.27260000	2.77370000	-0.21360000
C	-0.38240000	4.29150000	-0.16700000
C	0.95790000	4.17070000	-0.34870000

H	-0.98660000	5.18620000	-0.20020000
H	1.68090000	4.94780000	-0.54820000
C	-2.86230000	1.43270000	-0.02720000
C	-3.09650000	-1.03590000	-0.33050000
C	-4.03950000	0.90850000	0.55140000
C	-4.16610000	-0.45390000	0.38840000
H	-4.69430000	1.51540000	1.16250000
H	-4.93280000	-1.05690000	0.85670000
C	2.58170000	2.26130000	-0.28580000
C	-2.26400000	2.67480000	0.15550000
C	-2.69070000	-2.38200000	-0.27680000
C	2.44880000	-2.55490000	0.17950000
H	3.16710000	-3.34300000	0.37740000
H	-3.42780000	-3.10930000	0.04910000
H	-2.90080000	3.49570000	0.47130000
H	3.35570000	2.98910000	-0.50210000
S	-0.01520000	-1.75860000	-0.66540000
S	-2.08140000	0.20690000	-0.97880000
N	0.13620000	2.05510000	-0.00180000

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