Electronic Supplementary Material (ESI) for Dalton Transactions.

Supporting Information

Synthesis, Characterization and Crystal Structure Analysis of Cobaltaborane and Cobaltaheteroborane Clusters

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Contents:

Table S1 Selected bond parameters in Å for compound **1'**, optimized at B3LYP/ (SDD, 6-31g*) level of theory.

Atom pair	Expt.	Calc.
Co1-B1	1.956	1.941
Co1-B2	2.108	2.126
Co1-B3	3.262	3.269
Co1-B5	2.094	2.126
Co1-B6	1.982	1.941
Co2-B3	2.077	2.095
Co2-B4	1.984	2.011
Co2-B5	2.109	2.110
Co3-B1	2.023	1.969
Co3-B2	2.143	2.110
Co3-B3	2.146	2.095
Co3-B4	2.021	2.011
Co4-B1	2.190	2.234
Co4-B4	2.218	2.166
Co4-B6	2.148	2.235
Co1-Co4	2.606	2.635
Co2-Co4	2.586	2.586
Co2-Co4	2.639	2.586

Table S2 DFT calculated and experimental ^{11}B and ^{1}H chemical shifts (δ, ppm) for **1'-3'**and **5'**.

	Atom	Expt.	Calc.
1'	B1	125.4	141.8
	B6	125.4	141.8
	B4	125.4	100.5
	B3	33.6	35.9
	B2	33.6	34.0
	B5	33.6	34.0
2'	B1	75.7	62.4
	B2	75.7	62.4
3'	B1	22.0	24.0
	B2	22.0	24.0
5'	B1	43.0	51.9
	B2	43.0	51.9
	B1’	11.8	14.3
	B2’	11.8	14.3

Table S3 Frontier molecular orbital energies, E_{HOMO} and E_{LUMO} and HOMO-LUMO gaps (ΔE, eV) of the model compounds **1'**, **1a**, **1b, 5'**and **4'**.

Parameters	**1'**	**1a**	**1b**	**5'**	**4'**
E_{LUMO}(eV)	-2.43	-3.44	-2.08	-3.44	-2.76
E_{HOMO}(eV)	-5.69	-5.53	-5.43	-5.30	-4.84
$\Delta E = E_{LUMO} - E_{HOMO}$ (eV)	3.25	3.43	3.35	1.85	2.08
Energy(Hartree)	-1544.06	-1510.32	-1369.38	-11065.19	-781.78

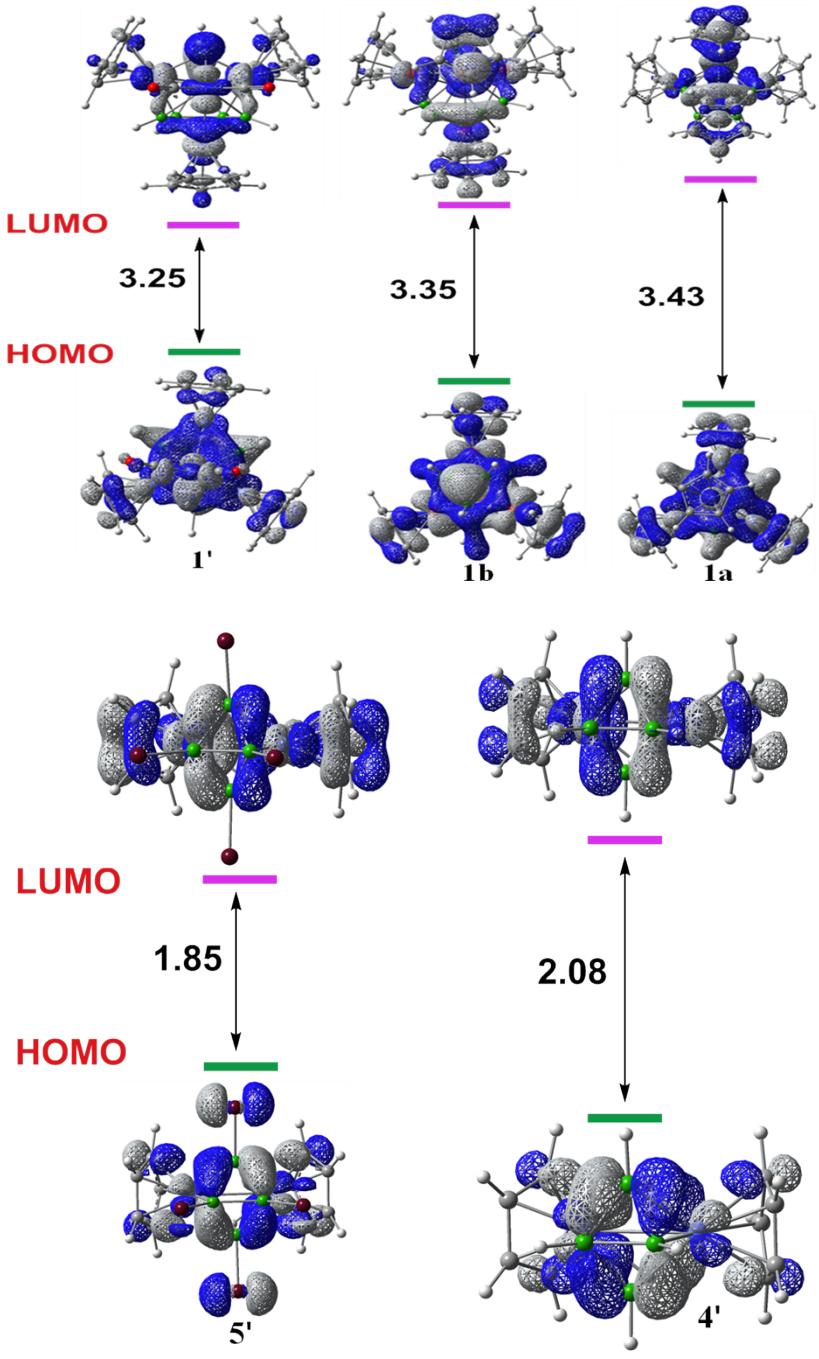

Table S4 Selected bond parameters in Å for optimized geometry of **5'**at B3LYP/ (SDD, 6-31g*) level of theory.

Atom Pair	Expt.	Calc.
Co1-Co1'	2.593	2.605
Co1-B1	2.030	2.019
Co1-B2	2.127	2.152
Co1-B2'	2.118	2.151
Co1'-B1'	2.030	2.091
Co1'-B2	2.118	2.152
Co1'-B2'	2.127	2.151
B1-B1'	1.695	1.692
B1-B2	1.722	1.731
B1-B2'	1.715	1.731
B2-B1'	1.715	1.731
B1'-B2'	1.722	1.731

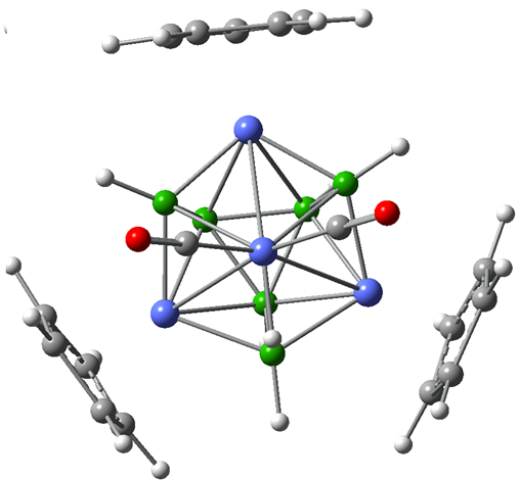

Fig. S1 Optimized structure of **1'** at B3LYP/ (SDD, 6-31g*) Level (Co blue, B green, O red, C gray)

Cartesian coordinates for the calculated structure of **1'**

B	0.00120100	1.16846200	-1.47035600	H	-4.26765800	0.03878000	-1.22772300
H	0.00203900	1.94497400	-2.38674300	H	-2.73370600	3.04868900	1.53005700
B	0.00211000	1.88874100	0.17757000	H	-2.09641500	3.81359500	-0.97208100
H	0.00329500	3.06652600	0.39460800	H	-3.01987400	1.94162000	-2.67730600
B	-0.88061100	-0.36879600	-1.62183600	H	-2.18509900	-3.59194400	-1.37651300
H	-1.47306700	-0.64438300	-2.62991400	H	-0.00368400	-3.39062900	-2.94886000
B	-1.56259500	-0.88719200	0.08014800	H	-1.35348400	-3.87035500	1.17028600
H	-2.55644000	-1.45991400	0.25102300	H	1.34467300	-3.87337900	1.17041100
O	2.15344900	-0.62188600	3.12715800	H	2.17714000	-3.59659400	-1.37630000
O	-2.15413000	-0.61919500	3.12668400	H	4.26932900	0.02975600	-1.22463500
Co	0.00027300	0.00438700	1.24663400	H	4.07767500	0.70811600	1.37306100
Co	-0.00216900	-1.95744800	-0.51367400	H	3.02585300	1.93267600	-2.67783600
Co	-1.75606000	1.05602700	-0.33382300	H	2.73749500	3.04560100	1.52782800
Co	1.75843800	1.05222000	-0.33416300	H	2.10367900	.80823000	-0.97594200
H	-4.07733100	0.71344200	1.37101300	H	0.00113100	1.50081900	1.55272600

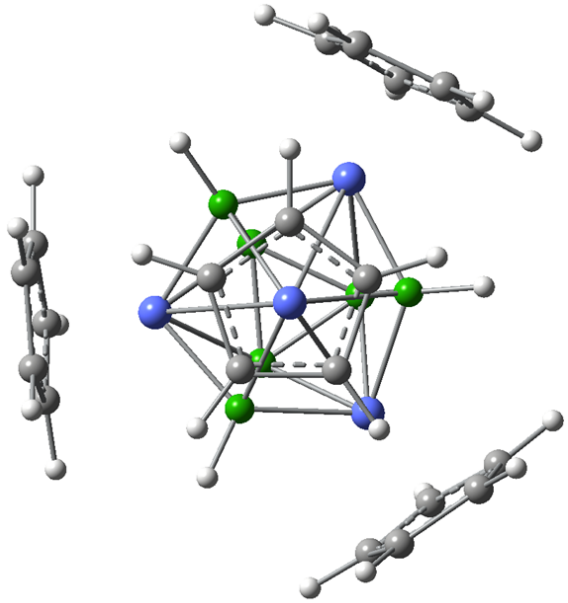

Fig. S2 Optimized structure of **1a** at B3LYP/ (SDD, 6-31g*) Level (Co blue, B green)

Cartesian coordinates for the calculated structure of **1a**

B	0.82695100	1.54163900	-0.02764400	H	0.90582900	-1.47069300	-2.63056900
B	-1.75292500	-0.05564000	-0.02063000	H	1.51060200	-2.44417000	0.39414300
B	-1.02563900	-0.03363400	-1.65410800	H	-3.15447500	2.66991400	1.29604900
B	0.47995100	0.89967000	-1.65848800	H	-3.81137500	1.95256200	-1.21309500
B	0.53465700	-0.86968600	-1.65783800	H	-0.85312900	4.08605500	1.18072000
B	0.92401400	-1.48902300	-0.02877400	H	-0.09715400	4.23454300	-1.39418000
C	-1.39737000	3.68049700	0.33827800	H	-1.91160400	2.89902300	-2.87543400
C	-2.61090800	2.93395900	0.39825200	H	-0.33819300	2.27189000	2.88873300
C	-2.96457900	2.56086100	-0.92642700	H	-2.25731000	0.37126700	2.89208600
C	-1.95781400	3.05911500	-1.80681200	H	-1.04236200	-2.03177500	2.90375600
C	-0.99950400	3.76864800	-1.02255900	H	1.61812500	-1.62499300	2.87746400
C	-2.78652300	-2.74835100	-0.96064200	H	2.05055800	1.04173900	2.87919700
C	-1.72668200	-3.20269700	-1.80127200	H	3.96417000	-1.18199200	1.27462700
C	-0.75139900	-3.83803700	-0.97533900	H	3.58910600	2.27587600	-1.35811000
C	-1.19259600	-3.74593700	0.37180900	H	3.87684300	1.51901900	1.20513700
C	-2.44971200	-3.07202600	0.38096500	H	3.47606000	0.05079300	-2.87740600
C	3.84098400	0.85626600	0.35063900	H	3.73197900	-2.08373600	-1.25054700
C	3.69628700	1.25986300	-1.00361300	H	-3.03313300	-2.81799000	1.25628600
C	3.63281400	0.08261500	-1.80781400	H	-3.65946200	-2.19809900	-1.28398500
C	3.77142000	-1.04679800	-0.94630100	H	-1.65929400	-3.06283500	-2.87159800
C	3.88687300	-0.56850800	0.38663800	H	0.18684000	-4.25759800	-1.31156700
C	1.08776400	0.55293700	2.91061500	H	-0.64881600	-4.09653600	1.23926300
C	-0.17620000	1.20398000	2.91598800	Co	-0.00005900	0.00165600	1.17298800
C	-1.19047800	0.19977200	2.91469100	Co	-0.95078000	-1.77234200	-0.47374800
C	-0.54804400	-1.07145500	2.92523100	Co	2.00887400	0.06220500	-0.47734100
C	0.85932000	-0.85609600	2.90858200	Co	-1.06102200	1.70793200	-0.47520900
H	1.35646600	2.52553300	0.40507400	Co	-0.00005900	0.00165600	1.17298800
H	-2.87357900	-0.09592400	0.40058000	Co	-0.95078000	-1.77234200	-0.47374800
H	-1.73525700	-0.05722100	-2.62360700				
H	0.81225200	1.52187800	-2.63169500				

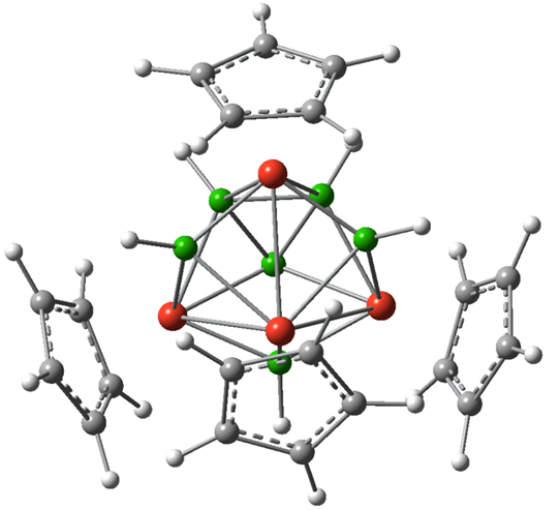

Fig.S3 Optimized structure of **1b** at B3LYP/ (SDD, 6-31g*) Level (Rh orange, B green, C gray)

Cartesian coordinates for the calculated structure of **1b**

B	1.82246700	0.21154500	-0.01272900	H	-0.68663800	-1.59996700	-2.69521400
B	-1.09499400	1.47610300	-0.02338600	H	-1.18182200	-2.73389500	0.35622900
B	-0.60749700	0.82071600	-1.73468600	Rh	0.84283300	1.94601800	-0.50511700
B	1.02056200	0.11649900	-1.73106300	Rh	-2.10540400	-0.24496500	-0.50800600
B	-0.40363400	-0.94205900	-1.73286800	Rh	1.26656900	-1.70191000	-0.50293200
B	-0.72752300	-1.68767400	-0.01847100	Rh	-0.00489700	0.00058400	1.28090500
C	2.34957700	3.58696900	0.31180100	H	0.50322600	4.49885900	1.20981600
C	1.03603300	4.15909300	0.33097300	H	-0.41263300	4.56903000	-1.32168900
C	0.55416700	4.20319700	-1.00231200	H	2.98296000	3.41844900	1.17309800
C	1.55354100	3.62593700	-1.85134000	H	3.59417700	2.81933200	-1.37946400
C	2.67683500	3.27662500	-1.03309500	H	1.48919900	3.51487000	-2.92559200
C	-4.17748900	0.67850700	-1.02863200	H	1.66065600	1.57961300	3.20912500
C	-3.91270300	-0.45975200	-1.85788200	H	-0.99962000	2.07752600	3.19256600
C	-3.91115900	-1.62214800	-1.02019000	H	-2.28719200	-0.29487500	3.20294200
C	-4.11705500	-1.19627000	0.31708300	H	-0.43219900	-2.25707700	3.19809500
C	-4.28196200	0.22692800	0.31197600	H	2.01056000	-1.09162500	3.21058400
C	3.11539200	-2.94920100	0.30906100	H	1.53477400	-4.25713100	1.22344200
C	3.35430400	-2.57919400	-1.03921900	H	4.14022800	-1.92597500	-1.39429600
C	2.33614000	-3.18104500	-1.84828600	H	3.69930500	-2.63630500	1.16506600
C	1.50137500	-3.96810700	-0.98999200	H	2.24149900	-3.09265600	-2.92240100
C	1.96964900	-3.80887800	0.33949800	H	0.64177000	-4.54700800	-1.30060800
C	1.05941500	-0.57695200	3.20805700	H	-4.45477200	0.85100500	1.17928000
C	0.87416700	0.83764400	3.20767000	H	-4.24296700	1.70461900	-1.36519200
C	-0.53386900	1.10150900	3.19613500	H	-3.78257700	-0.44845600	-2.93184800
C	-1.21521900	-0.15490800	3.20525800	H	-3.73955400	-2.63858800	-1.34869300
C	-0.23365700	-1.19369800	3.19902000	H	-4.14354200	-1.83745100	1.18880900
H	2.95224600	0.34373900	0.37191900				
H	-1.77744100	2.39083900	0.34992600				
H	-1.03329400	1.39424700	-2.69843200				
H	1.73231900	0.19799700	-2.69321400				

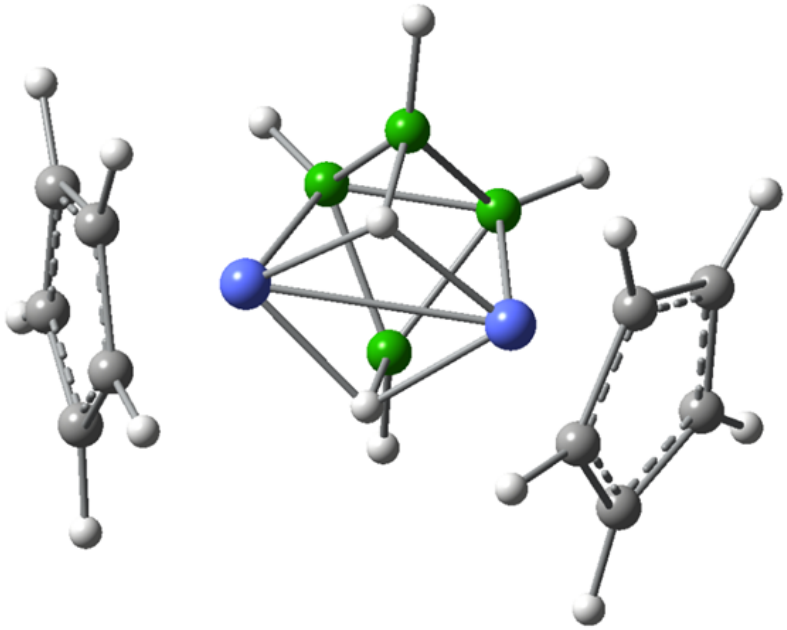

Fig. S4 Optimized structure of **4'**at B3LYP/ (SDD, 6-31g*) Level (Co blue, B green, C gray)

Cartesian coordinates for the calculated structure of **4'**

Co	-1.27553200	0.10598400	-0.00005000	H	-3.52934200	1.03643300	1.35602000
B	-0.84716300	2.08081300	0.00001400	H	-2.44497300	-1.31267400	2.20245600
B	0.00002700	1.24816200	-1.28447200	H	-1.76979100	-2.76456400	0.00868800
C	-3.17784000	0.22423700	0.71911600	H	-2.43815700	-1.32761500	-2.19702200
C	-3.17567600	0.21927400	-0.72648900	H	2.44271300	-1.31746900	-2.20073800
C	-2.60919300	-1.03021600	-1.16123000	H	1.76980000	-2.76458200	-0.00310600
C	-2.25954400	-1.78939600	0.00458700	H	2.44043100	-1.32281300	2.19876900
C	-2.61274000	-1.02231300	1.16414300	H	3.52659800	1.03010100	1.36548100
Co	1.27552900	0.10598100	0.00004400	H	3.52797500	1.03346100	-1.36055900
B	0.84716800	2.08080900	0.00004400	H	-0.00012200	-0.13700900	-1.08769900
B	-0.00003800	1.24811800	1.28450500	H	0.00013700	-0.13706700	1.08762900
C	3.17711700	0.22266200	-0.72152100	H	-0.00009500	1.36887300	2.48432500
C	3.17639900	0.22087000	0.72409200	H	0.00011100	1.36898500	-2.48428800
C	2.61038000	-1.02768900	1.16215000	H	1.63538400	2.99358100	0.00006600
C	2.25954800	-1.78940400	-0.00165400	H	-1.63537500	2.99358900	-0.00007100
C	2.61156000	-1.02484200	-1.16323500				
H	-3.52523900	1.02709500	-1.37000300				

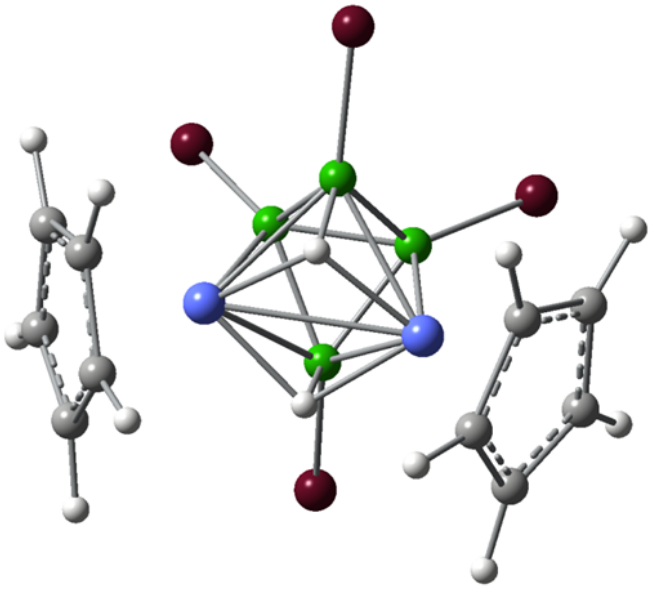

Fig. S5 Optimized structure of **5'**at B3LYP/ (SDD, 6-31g*) Level (Co blue, B green, Br brown, C gray)

Cartesian coordinates for the calculated structure of **5'**

Co	-1.30285400	0.00314100	1.10779100	H	-3.57582000	-1.35835600	0.26375600
Br	-2.05591500	-0.00346900	-2.37460900	H	-3.58144000	1.34050400	0.24269000
Br	-0.00255600	-3.19968600	-0.31418700	H	-2.43667300	2.19535800	2.53316500
B	-0.84626600	-0.00103900	-0.85914800	H	-1.72339000	0.02410500	3.96705700
B	-0.00093700	-1.27019500	-0.03882100	H	-2.42709700	-2.17233800	2.56719300
C	-3.22427900	0.71534900	1.04938300	H	2.43269200	-2.18168900	2.55129300
C	-3.22109400	-0.71905600	1.06039200	H	1.72413300	0.00273700	3.96740200
C	-2.61781300	-1.14615400	2.28137100	H	2.43149200	2.18614800	2.54909700
C	-2.24433300	0.01545400	3.01853200	H	3.57764900	1.35094500	0.25210000
C	-2.62275500	1.16397200	2.26350200	H	3.57845000	-1.34802200	0.25339000
Co	1.30264200	0.00124200	1.10811200	H	-0.00119100	-1.05696600	1.30095800
Br	2.05610500	-0.00578000	-2.37436400	H	0.00075100	1.06093400	1.2980550
Br	0.00253900	3.19805600	-0.32675500	H	3.57764900	1.35094500	0.25210000
B	0.84630400	-0.00223100	-0.85899900	H	3.57845000	-1.34802200	0.25339000
B	0.00093100	1.26973200	-0.04354600				
C	3.22259000	-0.71549500	1.05489400				
C	3.22217400	0.71896800	1.05422300				
C	2.62000700	1.15722600	2.27180000				
C	2.24469900	0.00233000	3.01863000				
C	2.62079600	-1.15297300	2.27295000				

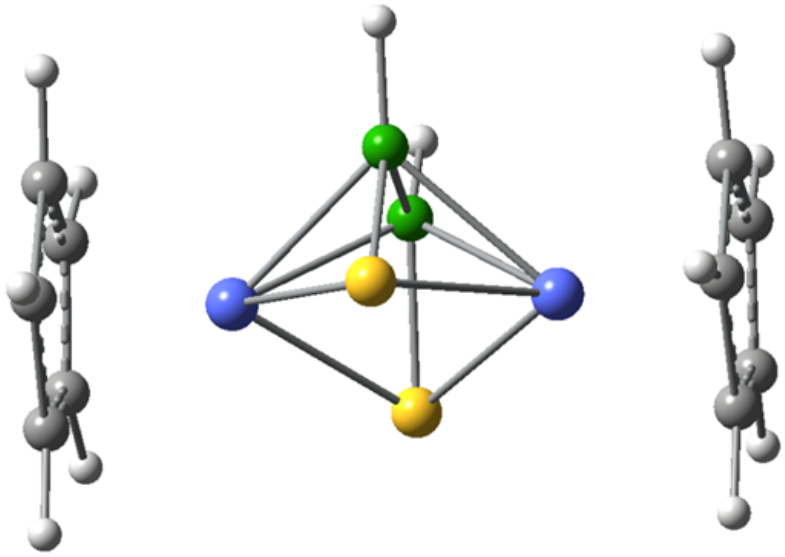

Fig. S6 Optimized structure of **3'**at B3LYP/ (SDD, 6-31g*) Level (Co blue, B green, S yellow, C gray)

Cartesian coordinates for the calculated structure of **3'**

C	3.26978500	1.14760000	-0.37309500
C	3.28253600	-0.00051900	-1.21900100
C	3.26976100	-1.14790900	-0.37205600
C	3.25388300	-0.71368300	0.98649100
C	3.25385100	0.71457500	0.98585300
C	-3.26978900	1.14738000	-0.37388800
C	-3.28249700	-0.00122100	-1.21910300
C	-3.26973500	-1.14812700	-0.37146800
C	-3.25393700	-0.71310300	0.98681200
C	-3.25386200	0.71515400	0.98532700
B	-0.00002000	0.86806300	1.17802300
H	-0.00004100	1.46613300	2.21125000
B	-0.00001500	-0.86810000	1.17800800
H	-0.00002300	-1.46618600	2.21122700
S	0.00000100	1.59870800	-0.49505300
S	0.00001400	-1.59872000	-0.49508600
Co	1.54657000	-0.00000400	-0.00864800
Co	-1.54657000	-0.00001800	-0.00869500
H	-3.21496400	1.35592600	1.85565100
H	-3.21502300	-1.35206600	1.85846400
H	-3.21979400	-2.17765300	-0.70155700
H	-3.27537800	-0.00235100	-2.30040800
H	-3.21984300	2.17622600	-0.70609000
H	3.21492000	1.35483200	1.85655500
H	3.21494600	-1.35316200	1.85776300
H	3.21985200	2.17664000	-0.70469600
H	3.27545400	-0.00100400	-2.30030600
H	3.21982900	-2.17724100	-0.70274900

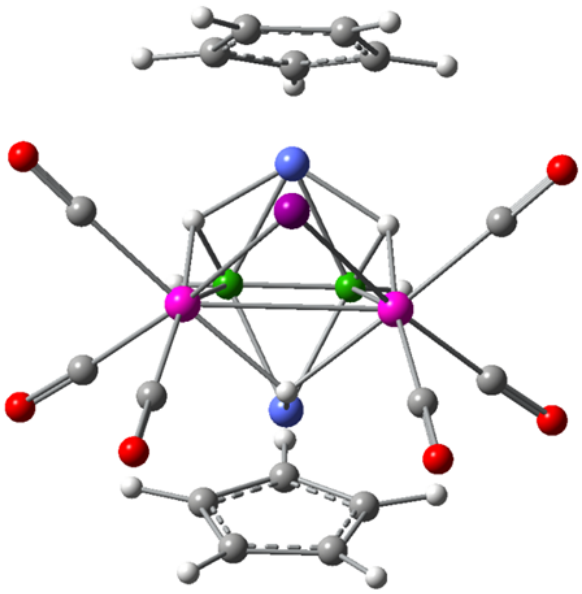

Fig. S7 Optimized structure of **2'**at B3LYP/ (SDD, 6-31g*, 3-21g) Level (Co blue, B green, I violet, Mo purple, O red, C gray)

Cartesian coordinates for the calculated structure of **2**

C	0.79233800	-1.94208800	-2.29333200	H	-0.52590200	-1.39232800	1.37327300
C	1.32900600	-2.93001900	0.12411800	H	-0.52636300	1.39293700	1.37304700
C	-1.30021400	-3.01088500	-0.41353400	H	1.27753600	-0.00011100	-0.70519700
C	-1.29937000	3.01140500	-0.41394000	H	3.65772000	-2.18132200	1.59412600
C	1.32946400	2.92998600	0.12322900	H	3.98832100	-1.34648400	-0.94881200
C	0.79309600	1.94060500	-2.29350400	H	3.98872800	1.34544000	-0.94927700
C	3.74093800	-1.15368100	1.27007800	H	3.65825600	2.18122800	1.59337300
C	3.63760500	0.00004900	2.10192700	H	3.46460600	0.00027900	3.16951900
C	3.74124200	1.15345700	1.26967100	H	-3.70589100	1.34540700	1.18942400
C	3.92212800	0.71003100	-0.07618000	H	-3.70756500	-1.34090400	1.18686300
C	3.92191200	-0.71074300	-0.07594400	H	-2.25835500	-2.17753100	3.31056500
C	-2.47385000	1.14635500	3.06292300	H	-2.25575400	2.17626100	3.31478400
C	-2.03337200	-0.00121600	3.78294700	H	-1.40353100	-0.00245500	4.66200500
C	-2.47523300	-1.14688100	3.06069300	H	-3.70756500	-1.34090400	1.18686300
C	-3.26003900	-0.70272600	1.93683200	H	-2.25835500	-2.17753100	3.31056500
Co	2.08680200	-0.00008800	0.72079800	B	0.61913900	0.87633100	1.87386800
Mo	0.05424000	-1.52398800	-0.47809000	Co	-1.25719000	0.00016500	1.84082000
I	-1.93916200	0.00026900	-1.89010700	Mo	0.05440900	1.52383500	-0.47807600
C	-3.25915700	0.70525400	1.93818700	H	0.97890500	1.61804100	2.73814100
O	1.26374500	-2.18089100	-3.32237800	H	0.97885600	-1.61649000	2.73900100
O	2.02990100	-3.80976300	0.41574100	B	0.61909300	-0.87503800	1.87449400
O	-2.08433800	-3.85922500	0.33210700				
O	-2.08302000	3.86019200	-0.33267000				
O	2.03056600	3.80970300	0.41442800				
O	1.26478500	2.17851200	-3.32260200				