Electronic Supplementary Information for Dalton Transactions

Supplementary Information

Supraicosahedral indenyl cobaltacarboranes

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Table S1 Computational model for 4-(η-$C_{10}H_8$)-4,1,6-*closo*-$FeC_2B_{10}H_{12}$ at minimum energy.

BP86 Energy	=	-841.996509	
Enthalpy 0K	=	-841.680167	
Enthalpy 298K	=	-841.662060	
Free Energy 298	=	-841.722772	
C	-0.49535	-0.72698	1.49620
B	-2.09529	-1.41767	1.34650
B	-3.40740	-1.22508	0.11578
B	-2.69003	-0.96207	-1.50640
B	-1.70405	0.53951	-1.34514
B	-3.33334	0.42497	-0.61189
B	-3.12359	0.18107	1.12264
B	-2.06368	1.30680	0.24442
Fe	0.00265	0.54282	-0.01026
B	-1.46623	0.45766	1.73004
B	-0.41133	-1.63367	0.25203
B	-2.00235	-2.13284	-0.41639
C	-1.02587	-0.99608	-1.21183
H	-1.36057	1.07099	2.76148
H	-2.31258	-2.16808	2.25542
H	0.42397	-2.49144	0.17223
H	0.16657	-0.99683	2.32531
H	-3.94892	0.54939	1.91203
H	-1.96394	-3.28745	-0.72782
H	-2.14341	2.50355	0.35379
H	-0.42924	-1.36549	-2.05303
H	-4.27766	1.01703	-1.05306
H	-3.08853	-1.30616	-2.58020
H	-1.51469	1.16095	-2.35604
H	-4.41814	-1.84643	0.28269
C	2.11872	0.27784	-0.82861
C	1.25419	1.14943	-1.58373
C	0.63989	2.28813	-0.99237
C	0.72401	2.47903	0.41457
C	1.41557	1.52670	1.20315
C	2.20767	0.47502	0.60477
H	1.08232	0.93805	-2.64324
H	-0.00211	2.93442	-1.59425
H	0.14421	3.26896	0.89657
H	1.36637	1.59377	2.29391
C	2.98979	-0.43472	1.38196
C	2.82180	-0.81892	-1.42291
C	3.58816	-1.66389	-0.64104
C	3.67209	-1.47159	0.76983
H	2.75691	-0.96064	-2.50656
H	4.13497	-2.49039	-1.10512
H	4.28358	-2.15193	1.37038
H	3.05441	-0.28295	2.46435

Table S2 Computational model for 4-(η-$C_{10}H_8$)-4,1,8-*closo*-$FeC_2B_{10}H_{12}$ at minimum energy.

BP86 Energy	=	-841.997556	
Enthalpy 0K	=	-841.680982	
Enthalpy 298K	=	-841.662962	
Free Energy 298K	=	-841.723264	
C	1.42649	1.00232	-1.38527
B	0.91673	-0.41524	-1.73472
B	2.06082	1.46254	-0.04709
Fe	-0.00411	0.60285	0.01547
B	2.80062	-0.00307	-1.24531
B	0.41579	-1.50619	-0.36727
B	1.74012	0.49449	1.43817
B	3.26824	0.26584	0.56278
C	1.93114	-1.64193	-1.13325
B	0.79140	-1.01004	1.28543
B	3.25520	-1.34336	-0.12290
B	1.79454	-2.22852	0.43811
B	2.58052	-1.04905	1.50937
H	1.31478	1.74711	-2.17965
H	0.43835	-0.63862	-2.81402
H	2.33433	2.62961	0.07277
H	3.57086	0.13485	-2.15218
H	-0.47227	-2.22504	-0.73686
H	1.66425	1.19490	2.41573
H	4.31208	0.78407	0.84916
H	2.08984	-2.39589	-1.90842
H	0.07109	-1.36551	2.18113
H	4.26353	-1.92825	-0.39003
H	1.81181	-3.41306	0.60369
H	3.09315	-1.43821	2.52043
C	-1.50454	1.56347	-1.17377
C	-2.17683	0.43083	-0.60518
C	-2.05113	0.20216	0.82423
C	-1.26960	1.12452	1.61333
C	-0.74275	2.31306	1.04785
C	-0.85451	2.52494	-0.35324
H	-1.49579	1.68117	-2.26161
C	-2.90394	-0.51566	-1.40133
C	-2.66011	-0.96656	1.39393
H	-1.08648	0.89282	2.66542
H	-0.14637	2.99332	1.65977
H	-0.33251	3.36798	-0.81373
C	-3.36966	-1.84046	0.59823
C	-3.49046	-1.61458	-0.81043
H	-2.55871	-1.13876	2.46918
H	-3.84381	-2.72090	1.04255
H	-4.05547	-2.32590	-1.42087
H	-2.99056	-0.33943	-2.47804

Table S3 Computational model for 4-(η-$C_{10}H_8$)-4,1,10-*closo*-$FeC_2B_{10}H_{12}$ at minimum energy.

BP86 Energy =	-841.995486		
Enthalpy 0K =	-841.679267		
Enthalpy 298K =	-841.661138		
Free Energy 298K =	-841.722046		
C	-1.50698	1.11022	1.28899
B	-0.99705	-0.25099	1.80507
B	-2.09018	1.43025	-0.10562
Fe	0.00400	0.61302	-0.01956
B	-2.89025	0.05931	1.15526
B	-0.46563	-1.45426	0.56533
B	-1.63752	0.33752	-1.47721
B	-3.22985	0.18744	-0.73092
B	-2.03833	-1.64626	1.34687
C	-0.82406	-1.07503	-1.04293
B	-3.27940	-1.35657	0.12501
B	-1.78642	-2.27483	-0.26319
B	-2.48824	-1.20588	-1.47891
H	-1.45765	1.94685	1.99436
H	-0.51386	-0.30444	2.90686
H	-2.36440	2.57483	-0.36154
H	-3.73707	0.40435	1.93183
H	0.52220	-2.08558	0.82193
H	-1.42906	0.86466	-2.53694
H	-4.21356	0.69469	-1.19283
H	-2.22131	-2.38146	2.27647
H	-0.11783	-1.46482	-1.78299
H	-4.34680	-1.87951	0.27308
H	-1.64978	-3.42999	-0.54331
H	-2.80120	-1.67858	-2.53229
C	1.47267	1.53524	1.19118
C	2.17214	0.41852	0.61748
C	2.07121	0.21134	-0.81618
C	1.29504	1.13985	-1.60195
C	0.75559	2.32184	-1.03402
C	0.84326	2.51326	0.37206
H	1.43200	1.63077	2.27985
C	2.88890	-0.53426	1.41190
C	2.68274	-0.95232	-1.38999
H	1.12612	0.92196	-2.66032
H	0.17105	3.01038	-1.64811
H	0.31137	3.34737	0.83679
C	3.37609	-1.84087	-0.59283
C	3.48092	-1.62989	0.81788
H	2.61030	-1.10625	-2.47159
H	3.85416	-2.71727	-1.04108
H	4.03429	-2.34984	1.42835
H	2.95633	-0.37282	2.49204

Table S4 Computational model for 4-(η-$C_{10}H_8$)-4,1,12-*closo*-$FeC_2B_{10}H_{12}$ at minimum energy.

BP86 Energy =	-841.999364		
Enthalpy 0K =	-841.682752		
Enthalpy 298K =	-841.664705		
Free Energy 298K =	-841.725126		
C	-1.42988	0.99369	1.39442
B	-0.89202	-0.40942	1.76117
B	-2.09363	1.44447	0.07408
Fe	0.00954	0.59863	-0.01540
B	-2.82393	-0.02875	1.25824
B	-0.42800	-1.49732	0.41721
B	-1.73104	0.50728	-1.43128
B	-3.27685	0.26639	-0.58709
B	-1.97941	-1.73978	1.24442
B	-0.78804	-0.98214	-1.26170
B	-3.26818	-1.33021	0.12144
C	-1.78914	-2.06936	-0.38637
B	-2.55796	-1.03638	-1.50833
H	-1.33790	1.75565	2.17589
H	-0.37357	-0.56346	2.83744
H	-2.38100	2.60902	-0.04163
H	-3.62875	0.21473	2.11315
H	0.47127	-2.26704	0.61658
H	-1.65577	1.19434	-2.41714
H	-4.30734	0.77605	-0.92842
H	-2.14098	-2.64295	2.01227
H	-0.09888	-1.45469	-2.12424
H	-4.26452	-1.97912	0.24426
H	-1.78530	-3.12532	-0.66660
H	-3.02074	-1.53239	-2.49322
C	1.49088	1.55130	1.18433
C	2.17114	0.42503	0.60942
C	2.06078	0.21230	-0.82327
C	1.27524	1.13567	-1.60607
C	0.73918	2.31787	-1.03245
C	0.84817	2.52257	0.36926
H	1.46882	1.65392	2.27327
C	2.89513	-0.52668	1.40260
C	2.68097	-0.94672	-1.39970
H	1.09807	0.91343	-2.66151
H	0.14117	2.99946	-1.64134
H	0.32274	3.36050	0.83472
C	3.38784	-1.82561	-0.60668
C	3.49445	-1.61509	0.80545
H	2.59339	-1.10641	-2.47838
H	3.87268	-2.69751	-1.05654
H	4.05724	-2.33019	1.41339
H	2.96803	-0.36276	2.48212

Table S5 Computational model for 4-(η-$C_{10}H_8$)-4,1,2-*closo*-$FeC_2B_{10}H_{12}$ at minimum energy.

BP86 Energy	=	-841.982006	
Enthalpy 0K	=	-841.665795	
Enthalpy 298K	=	-841.647740	
Free Energy 298K	=	-841.708158	
C	1.40857	0.74699	-1.47786
C	0.68037	-0.49398	-1.59339
B	2.09987	1.33238	-0.13304
Fe	-0.00872	0.57547	0.00823
B	3.04396	0.11437	-1.12355
B	0.46375	-1.58563	-0.42754
B	1.70843	0.48339	1.42678
B	3.30913	0.33801	0.63734
B	2.07667	-1.60025	-1.30115
B	0.84416	-1.05519	1.26746
B	3.33425	-1.29182	-0.11700
B	1.87790	-2.21676	0.37700
B	2.60874	-1.05127	1.49918
H	1.30273	1.47280	-2.29288
H	0.07215	-0.64458	-2.49261
H	2.28439	2.51857	-0.22473
H	3.78455	0.45764	-2.00194
H	-0.43700	-2.33313	-0.70394
H	1.57195	1.18601	2.39538
H	4.27612	0.89624	1.07514
H	2.25819	-2.24261	-2.29682
H	0.09358	-1.44046	2.12630
H	4.37422	-1.85206	-0.32612
H	1.87744	-3.38701	0.63950
H	3.10125	-1.42860	2.52529
C	-1.52072	1.59787	-1.13742
C	-2.21057	0.46796	-0.57268
C	-2.05922	0.20495	0.84661
C	-1.22532	1.08637	1.62731
C	-0.68213	2.27594	1.07047
C	-0.82809	2.52644	-0.32105
H	-1.54264	1.73931	-2.22297
C	-2.97328	-0.44603	-1.37065
C	-2.68113	-0.95925	1.40773
H	-1.01594	0.83004	2.66846
H	-0.04938	2.92283	1.68164
H	-0.30233	3.36925	-0.77765
C	-3.42674	-1.80290	0.61040
C	-3.57154	-1.54578	-0.78863
H	-2.55735	-1.15592	2.47633
H	-3.90823	-2.68296	1.04711
H	-4.16500	-2.23143	-1.40135
H	-3.08751	-0.24382	-2.44064

Table S6 Computational model for 4-(η-C_9H_7)-4,1,6-*closo*-$CoC_2B_{10}H_{12}$ at τ = –42.3 º.

BP86 Energy =	-825.221223		
Enthalpy 0K =	-824.922569		
Enthalpy 298K =	-824.904196		
Free Energy 298K =	-824.964542		
Co	-0.05703	0.48956	-0.01040
C	0.37689	-1.01572	1.25520
H	-0.34369	-1.48585	1.93123
B	0.46853	-1.64287	-0.15269
H	-0.28026	-2.51759	-0.48685
B	1.22006	0.14750	1.83393
H	0.99095	0.51031	2.95710
B	2.03954	-1.54031	1.12938
H	2.25509	-2.44777	1.88136
C	1.15254	-0.69128	-1.40672
H	0.65286	-0.92494	-2.35244
B	1.84674	1.34267	0.59906
H	1.77661	2.48892	0.95479
B	2.92957	0.13950	1.32686
H	3.65733	0.40437	2.24302
B	2.15313	-1.88250	-0.74872
H	2.25042	-2.95252	-1.27439
B	1.68309	0.89166	-1.16225
H	1.49391	1.70635	-2.02252
B	3.41869	-0.99921	0.08759
H	4.46925	-1.55798	0.22525
B	2.81661	-0.46324	-1.51496
H	3.34115	-0.54529	-2.58606
B	3.24480	0.75735	-0.29947
H	4.15885	1.50115	-0.51844
C	-2.12863	0.44973	-0.82472
C	-1.26601	1.49747	-1.33792
H	-0.99793	1.65117	-2.38334
C	-0.86558	2.33586	-0.24188
H	-0.23282	3.21917	-0.31331
C	-1.34094	1.73528	0.97501
H	-1.15264	2.10145	1.98411
C	-2.18417	0.60288	0.62022
C	-2.94414	-0.30974	1.40353
H	-2.99799	-0.19556	2.49039
C	-3.63252	-1.32491	0.75164
H	-4.23977	-2.02511	1.33399
C	-3.57629	-1.47744	-0.66793
H	-4.13813	-2.29175	-1.13558
C	-2.82981	-0.61525	-1.45888
H	-2.79547	-0.73071	-2.54644

Table S7 Spectral changes recorded in THF solution, both in OTTLE cell and in macroelectrolysis, consequent to the first cathodic reduction of the indenyl cobaltacarboranes under study. λ in nm.

Complex	λ_{max}	λ (isosbestic)	color
4-(η-C_9H_7)-4,1,6-*closo*-$CoC_2B_{10}H_{12}$ (**1**)	332		burnt orange
[4-(η-C_9H_7)-4,1,6-*closo*-$CoC_2B_{10}H_{12}$]$^-$ ([**1**]$^-$)	321, 383, 474 (broad)	379	orange
4-(η-C_9H_7)-4,1,8-*closo*-$CoC_2B_{10}H_{12}$ (**3**)	323		burnt orange
[4-(η-C_9H_7)-4,1,8-*closo*-$CoC_2B_{10}H_{12}$]$^-$ ([**3**]$^-$)	320, 385, 534 (broad)	368	carmine red
4-(η-C_9H_7)-4,1,10-*closo*-$CoC_2B_{10}H_{12}$ (**8**)	336		burnt orange
[4-(η-C_9H_7)-4,1,10-*closo*-$CoC_2B_{10}H_{12}$]$^-$ ([**8**]$^-$)	321, 390, 519 (broad)	376	red orange
4-(η-C_9H_7)-4,1,12-*closo*-$CoC_2B_{10}H_{12}$ (**9**)	321		burnt orange
[4-(η-C_9H_7)-4,1,12-*closo*-$CoC_2B_{10}H_{12}$]$^-$ ([**9**]$^-$)	320, 390, 581 (broad)	369	carmine red

Fig. S1 Perspective views of compound **4** (two independent molecules **A** and **B**). Displacement ellipsoids as for **1** (Fig. 2).

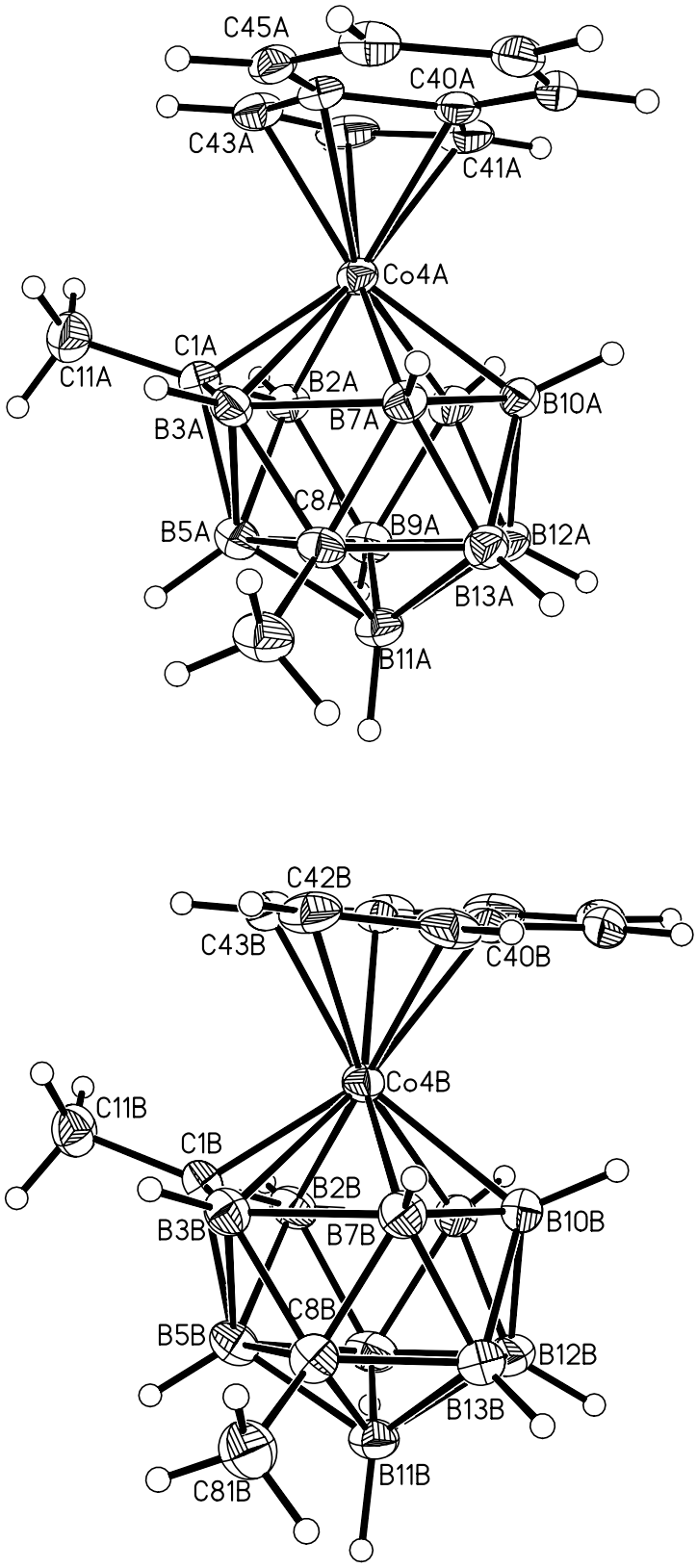

Fig. S2 Perspective view of compound **7**. Displacement ellipsoids as for **1**.

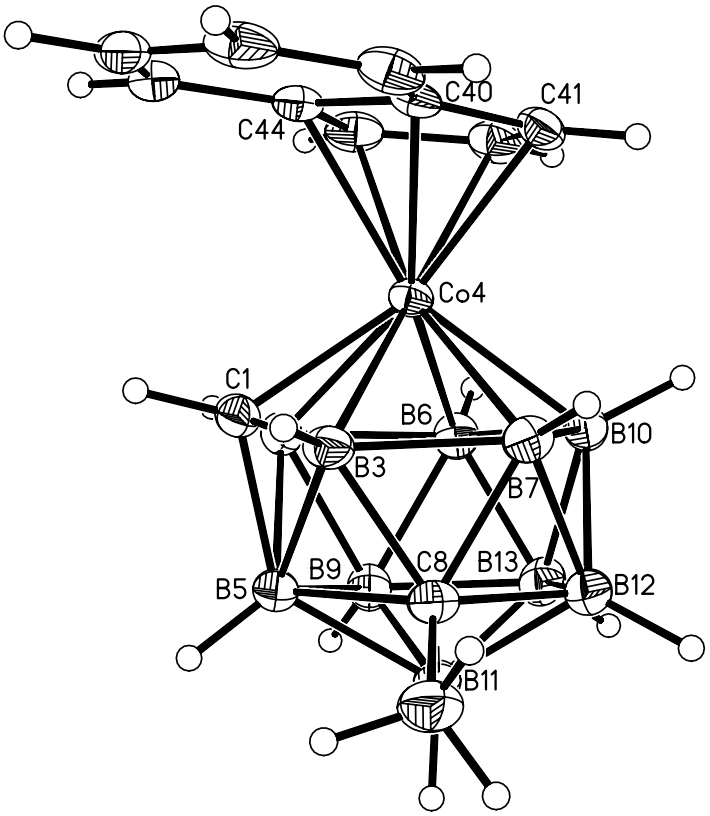

Fig. S3 Perspective view of compound **8**. Displacement ellipsoids as for **1**.

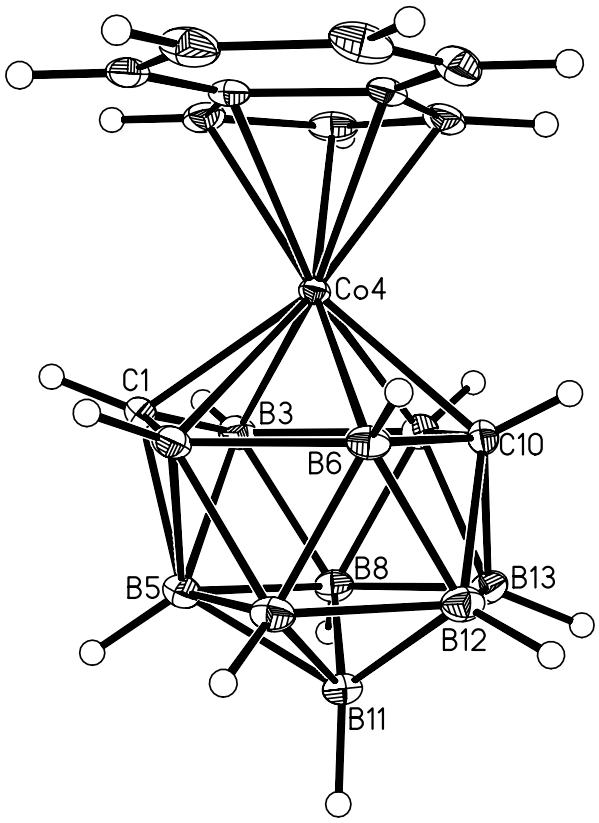

Fig. S4 Perspective view of compound **9**. The atom numbering reflects crystallographic symmetry (mirror plane through atoms Co4, C12 and B11). C1 and B3 are disordered across this plane, and in the Figure C1A and B3 are omitted for clarity. Displacement ellipsoids as for **1**.

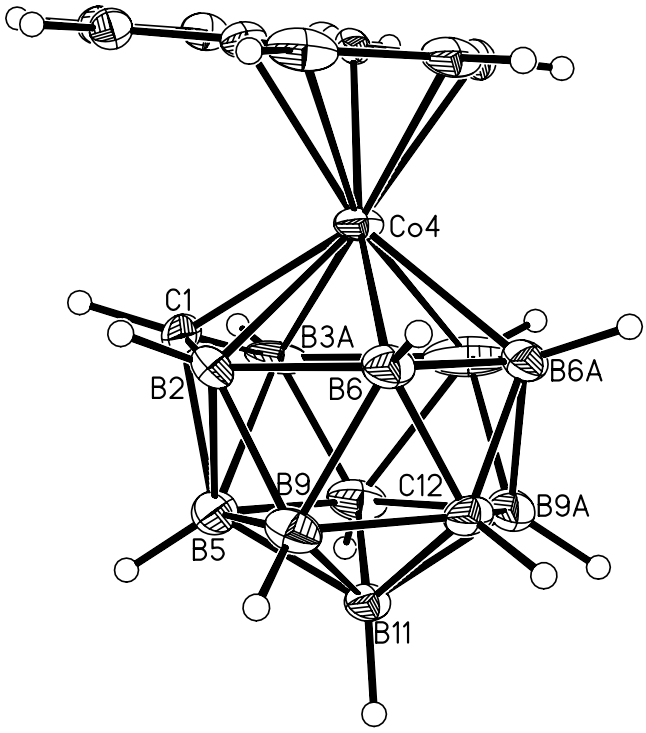

Fig. S5 Perspective view of compound **10**. Displacement ellipsoids as for **1**.

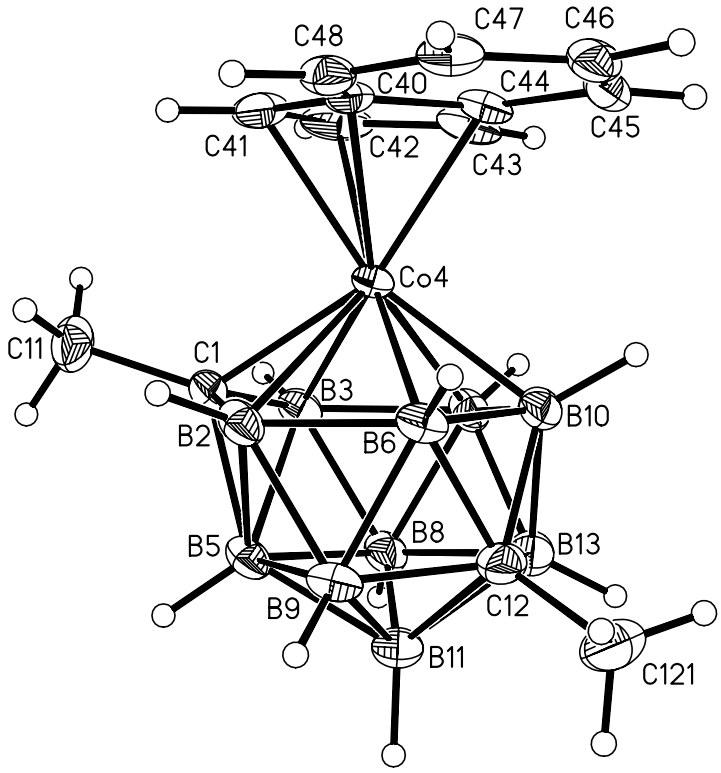

Fig. S6 Perspective view of compound **12**. Displacement ellipsoids as for **1**.

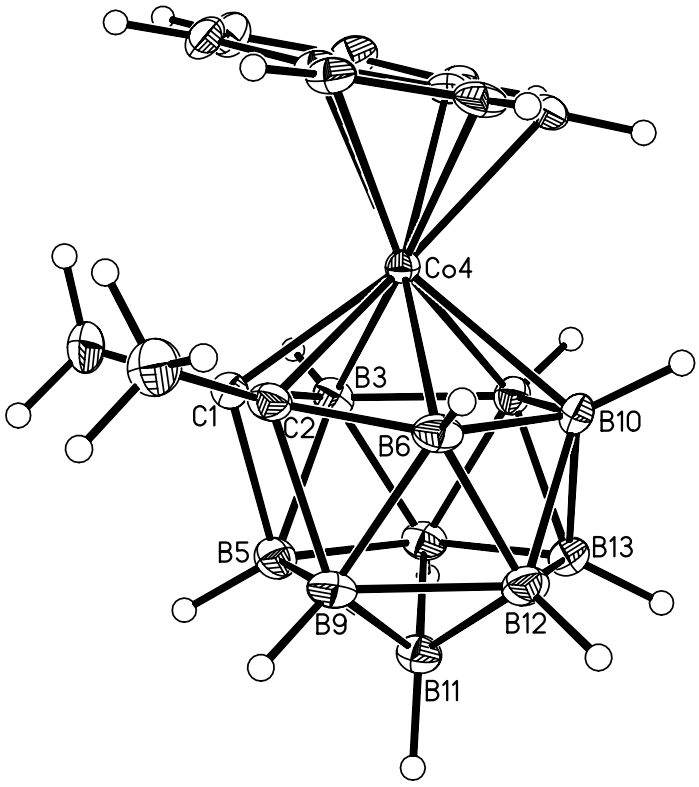

Fig. S7 Cyclic voltammetric response recorded at a gold electrode in THF solution of a mixture of equimolar amounts (2.3×10^{-3} mol dm^{-3}) of 1,2-*closo*-$C_2B_{10}H_{12}$ and $Fe(C_5H_5)_2$. $[NBu_4][PF_6]$ (0.2 mol dm^{-3}) supporting electrolyte. Scan rate 0.2 V s^{-1}. T = 293 K.

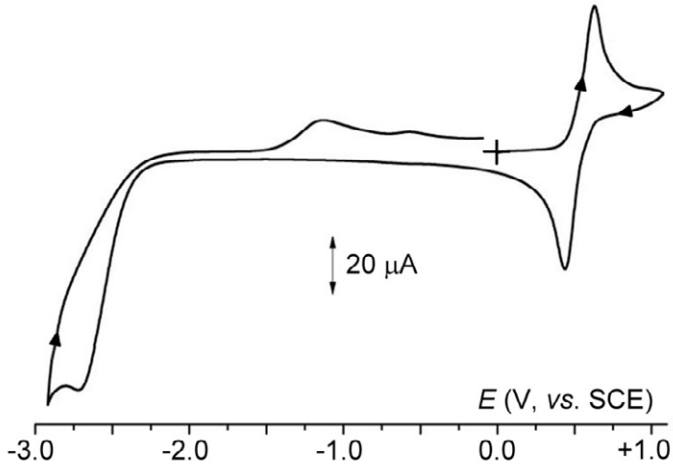

Fig. S8 Experimental second derivative X-band EPR spectrum of [4-(η-C_9H_7)-4,1,6-*closo*-$CoC_2B_{10}H_{12}]^-$ ([**1**]$^-$). THF solution. T = 105 K. ν = 9.467 GHz.