Supporting Information

syn-Permethylpentalene Iron and Cobalt carbonyl complexes – proximity bimetallics lacking metal-metal bonding

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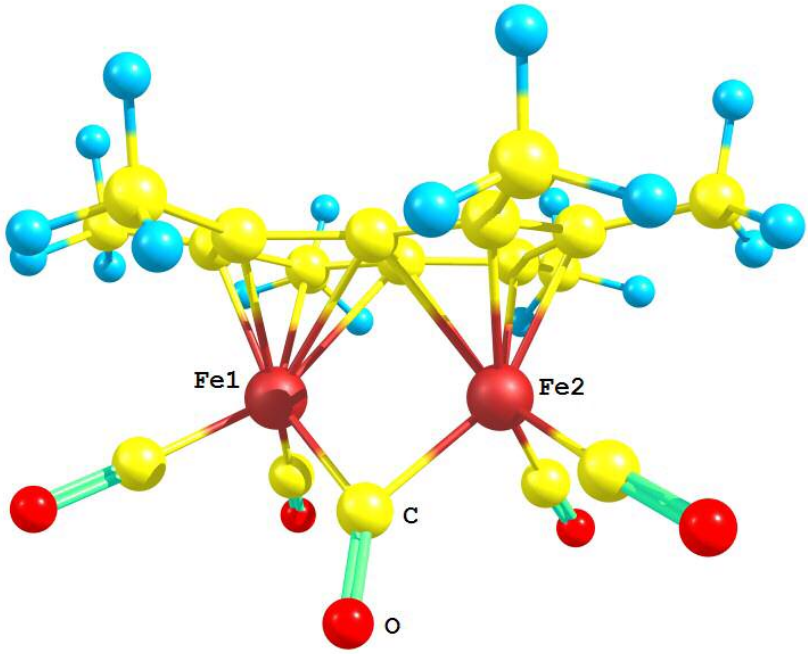
Calculated geometrical parameters for 1 [Pn*$Fe_2(CO)_5$].

Parameter	Distance /Å
Fe-Fe	2.64
Fe2-C_{br}	2.275, 2.324
Fe1-C_{br}	2.260, 2.268
Fe2-C_{α}	2.078, 2.087
Fe1-C_{α}	2.088, 2.089
Fe2-C_{β}	2.022
Fe1-C_{β}	2.031
Fe2-$CO_{(br)}$	1.903
Fe1-$CO_{(br)}$	1.927

Optimised structure of 1.



Cartesian coordinates for 1. 26 = Fe 6 = C, 8 = O, 1 = H

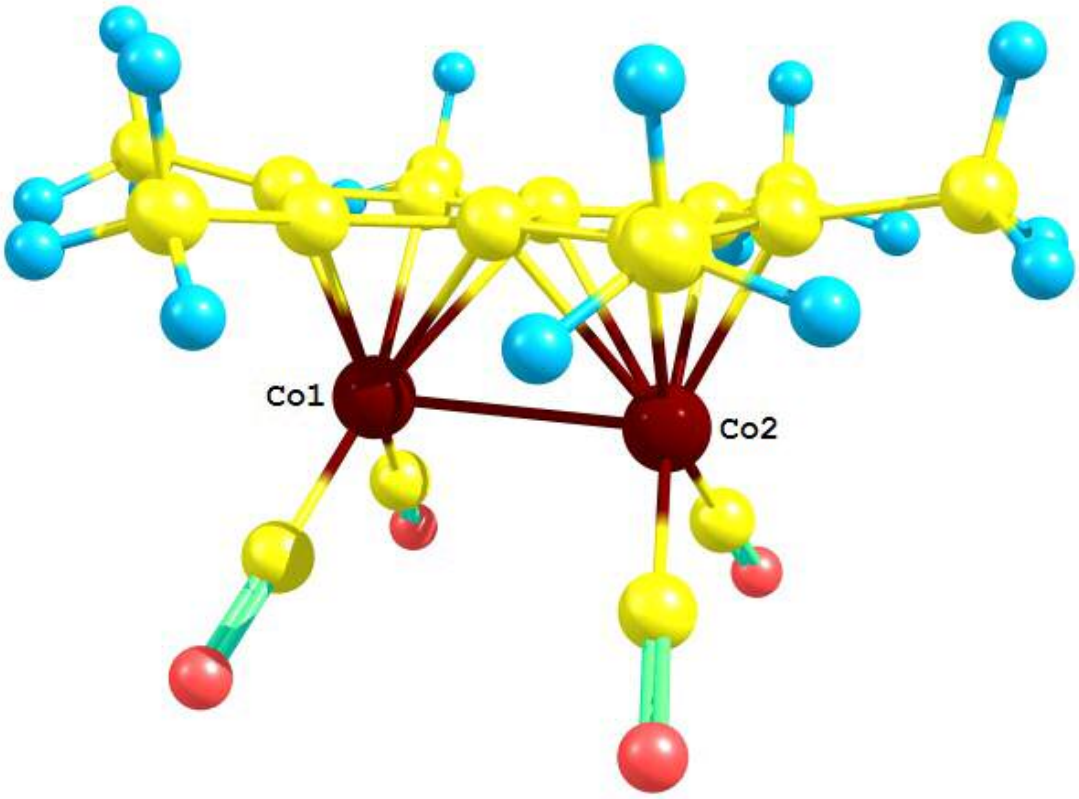
26	0.009867000	-0.000560000	1.307375000
26	-0.054897000	-0.015345000	-1.328946000
6	-1.728688000	-1.150834000	1.444281000
6	-1.791481000	0.052460000	2.244806000
6	-1.700509000	1.194198000	1.389190000
6	1.020320000	1.360001000	1.624396000
6	0.771608000	-0.998495000	2.468589000
6	1.178186000	-0.705148000	-0.054175000
6	-1.795806000	1.120027000	-1.334650000
6	-1.916069000	-0.069937000	-2.117806000
6	-1.754794000	-1.223420000	-1.259067000
6	0.908460000	1.377603000	-1.678360000
6	0.659898000	-0.953958000	-2.566499000
6	-1.754532000	-0.732688000	0.084017000
6	-1.872575000	-2.533761000	1.953722000
6	-2.022990000	0.083685000	3.703938000
6	-1.723917000	0.703493000	0.039714000
6	-1.799894000	2.610687000	1.808201000
8	1.644365000	2.299617000	1.887700000
8	1.226041000	-1.666390000	3.299089000
8	2.203076000	-1.291433000	-0.065990000
6	-1.968877000	2.508684000	-1.818788000

6	-2.249353000	-0.127730000	-3.556894000
6	-1.876950000	-2.638091000	-1.679054000
8	1.499607000	2.335203000	-1.951298000
8	1.099689000	-1.573246000	-3.441529000
1	-1.363844000	-3.257475000	1.298522000
1	-1.440632000	-2.639321000	2.961758000
1	-2.936492000	-2.824158000	2.013956000
1	-1.638735000	1.014554000	4.148901000
1	-1.527264000	-0.760371000	4.209732000
1	-3.102452000	0.022788000	3.932564000
1	-1.183208000	3.265290000	1.172356000
1	-1.460951000	2.746180000	2.847275000
1	-2.843049000	2.967761000	1.745462000
1	-1.728864000	2.590734000	-2.890369000
1	-1.313961000	3.211952000	-1.280446000
1	-3.010923000	2.847404000	-1.680423000
1	-1.750577000	-0.975646000	-4.053686000
1	-3.337934000	-0.246827000	-3.704759000
1	-1.938658000	0.792767000	-4.074963000
1	-1.230894000	-3.293008000	-1.073528000
1	-2.915766000	-2.999678000	-1.574326000
1	-1.582355000	-2.769045000	-2.732518000

Calculated and experimental geometrical parameters for 2 [cis-Pn*$Co_2(CO)_4$] in C_{2v} symmetry.

Parameter	Calculated	Experimental
Co1-Co2	2.64	2.675
Co1-C_{br}	2.25	2.287 / 2.275
Co1-C_{α}	2.04	2.070 / 2.082
Co1-C_{β}	1.99	2.039
Co1-$C_{(CO)}$	1.71	1.744 / 1.752
Co2-C_{br}	2.25	2.276 / 2.295
Co2-C_{α}	2.04	2.070 / 2.082
Co2-C_{β}	1.99	2.033
Co2-$C_{(CO)}$	1.71	1.750 / 1.745

Optimised structure of 2.



Cartesian coordinates for 2. 27 = Co, 6 = C, 8 = O 1 = H

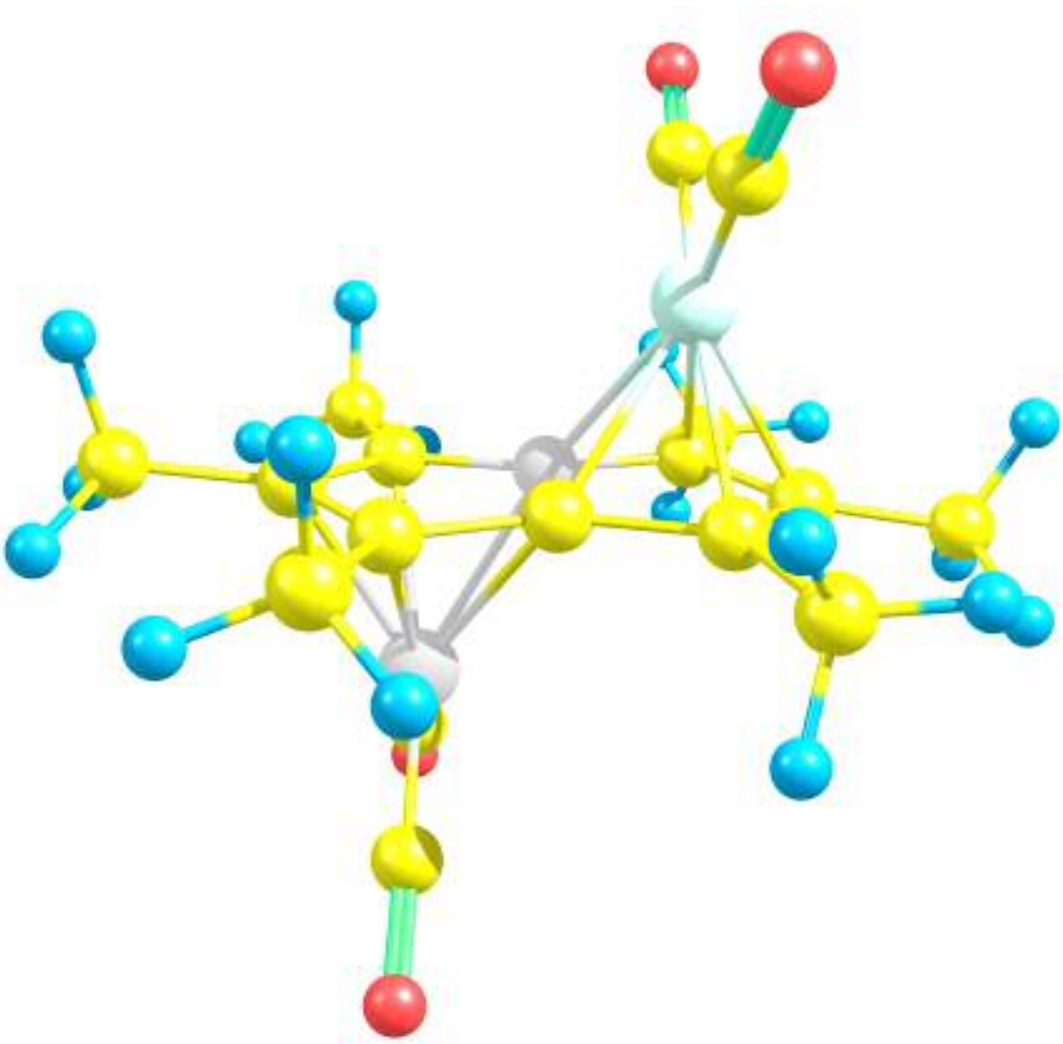
27	1.337155001	0.000000000	-0.407013273
27	-1.337155001	0.000000000	-0.407013273
6	1.378930624	-1.168048518	1.308870638
6	2.205880219	0.000000000	1.434249099
6	1.378930624	1.168048518	1.308870638
6	1.612785082	1.300234610	-1.538085570
6	1.612785082	-1.300234610	-1.538085570
6	-1.378930624	1.168048518	1.308870638
6	-2.205880219	0.000000000	1.434249099
6	-1.378930624	-1.168048518	1.308870638
6	-1.612785082	-1.300234610	-1.538085570
6	-1.612785082	1.300234610	-1.538085570
6	0.000000000	-0.711409344	1.301222220
6	1.835634310	-2.589101497	1.441140900
6	3.683937081	0.000000000	1.704685383
6	0.000000000	0.711409344	1.301222220
6	1.835634310	2.589101497	1.441140900
8	1.805730835	2.159773402	-2.271652970
8	1.805730835	-2.159773402	-2.271652970
6	-1.835634310	2.589101497	1.441140900
6	-3.683937081	0.000000000	1.704685383
6	-1.835634310	-2.589101497	1.441140900

8	-1.805730835	-2.159773402	-2.271652970
8	-1.805730835	2.159773402	-2.271652970
1	1.306639805	-3.204935717	0.934778183
1	2.751229792	-2.707857019	1.148266959
1	1.780322449	-2.896583096	2.358078561
1	4.124695892	0.758202117	1.344816497
1	4.124695892	-0.758202117	1.344816497
1	3.840037593	0.000000000	2.605442646
1	1.306639805	3.204935717	0.934778183
1	2.751229792	2.707857019	1.148266959
1	1.780322449	2.896583096	2.358078561
1	-2.751229792	2.707857019	1.148266959
1	-1.306639805	3.204935717	0.934778183
1	-1.780322449	2.896583096	2.358078561
1	-4.124695892	-0.758202117	1.344816497
1	-4.124695892	0.758202117	1.344816497
1	-3.840037593	0.000000000	2.605442646
1	-1.306639805	-3.204935717	0.934778183
1	-2.751229792	-2.707857019	1.148266959
1	-1.780322449	-2.896583096	2.358078561

Calculated geometrical parameters for *trans*-Pn*$Co_2(CO)_4$ in C_{2h} symmetry.

Parameter	Calculated
Co1-Co2	4.04
Co1-C_{br}	2.14
Co1-C_{α}	2.03
Co1-C_{β}	2.03
Co1-$C_{(CO)}$	1.71

Optimised structure of *trans*-Pn*$Co_2(CO)_4$.



Cartesian coordinates for *trans*-Pn*$Co_2(CO)_4$. 27 = Co, 6 = C, 8 = O 1 = H

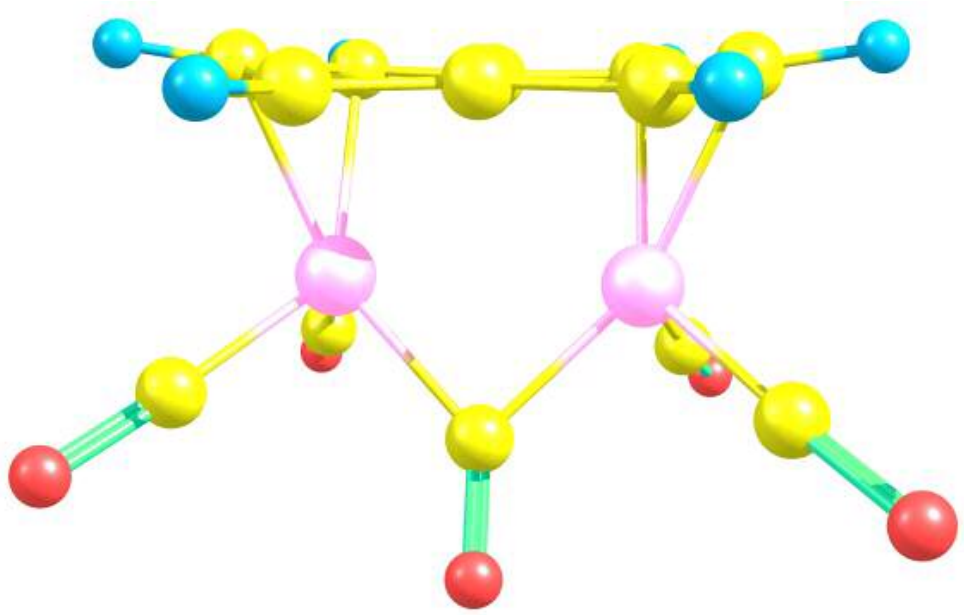
27	1.126972000	0.013416000	-0.822287000
6	1.256126000	-1.136669000	0.848708000
6	2.065029000	0.036308000	0.982046000
6	1.230497000	1.190288000	0.831319000
6	-0.137751000	0.726416000	0.756312000
6	-1.515623000	1.158411000	0.659384000
6	-2.320559000	-0.016953000	0.508206000
6	-1.489017000	-1.169321000	0.672204000
6	-0.121475000	-0.702896000	0.765369000
6	-1.917732000	-2.577517000	0.521436000
1	-1.566780000	-2.979099000	-0.447103000
1	-3.015011000	-2.664127000	0.549101000
1	-1.507664000	-3.222730000	1.315744000
6	-3.769689000	-0.036212000	0.186266000
1	-4.018142000	-0.907997000	-0.440120000
1	-4.053892000	0.864091000	-0.381224000
1	-4.405385000	-0.078259000	1.084204000
6	-1.975592000	2.554744000	0.492799000
1	-1.637560000	2.951354000	-0.482352000
1	-3.074518000	2.620300000	0.525869000
1	-1.574635000	3.217984000	1.276969000
6	1.663548000	2.598275000	0.954336000
1	1.039596000	3.269639000	0.343530000
1	2.711161000	2.726319000	0.640684000
1	1.582463000	2.931129000	2.004850000
6	3.519321000	0.053779000	1.245234000
1	3.993645000	0.945310000	0.806804000
1	4.012725000	-0.832742000	0.817993000
1	3.728600000	0.062798000	2.330612000
6	1.717253000	-2.533666000	0.992009000

1	2.767682000	-2.644969000	0.681365000
1	1.107561000	-3.225560000	0.389747000
1	1.641045000	-2.853620000	2.046992000
6	1.266962000	1.268816000	-1.966464000
8	1.386924000	2.130149000	-2.732605000
6	1.252865000	-1.255620000	-1.954547000
8	1.360104000	-2.123370000	-2.715042000
27	-1.402340000	0.004144000	2.330939000
6	-1.490698000	-1.271833000	3.458555000
8	-1.563681000	-2.165250000	4.192542000
6	-1.606726000	1.277268000	3.445873000
8	-1.774224000	2.161342000	4.176159000

Calculated geometrical parameters for *cis*- Pn*$Fe_2(CO)_5$.

Parameter	Calculated
Fe1-Fe2	2.78
Fe1-C_{br}	2.38 and 2.39
Fe1-C_{α}	2.14 and 2.15
Fe1-C_{β}	2.07
Fe1-$C_{(CO)}$	1.75 and 1.76
Fe1-$C_{(\mu\text{-}CO)}$	1.71

Optimised structure of *cis*-$PnFe_2(CO)_5$.



Cartesian coordinates for *cis*-$PnFe_2(CO)_5$. 27 = Co, 6 = C, 8 = O 1 = H

26	-2.058437000	-1.494859000	-0.137667000
6	-0.801818000	1.426199000	1.322861000
6	0.580587000	1.398906000	0.901086000
6	0.688422000	0.622996000	-0.297572000
6	1.379244000	-1.686645000	1.200087000
6	0.243612000	-0.447423000	3.114914000
6	-1.267149000	-1.978476000	1.596824000
6	-1.436681000	-0.292152000	-1.780154000
6	-2.815786000	-0.091545000	-1.451056000
6	-2.907914000	0.482980000	-0.126495000
6	-1.464775000	-2.962778000	-0.895888000
6	-3.571408000	-2.242381000	0.314856000
6	-1.574237000	0.813030000	0.284477000
6	-0.652033000	0.295645000	-0.722139000
8	2.300212000	-2.392077000	1.099068000
8	0.399577000	-0.331485000	4.262611000

8	-1.473700000	-2.815535000	2.410440000
8	-1.102298000	-3.915521000	-1.458148000
8	-4.603022000	-2.721586000	0.561095000
26	0.061270000	-0.544567000	1.380916000
1	-1.188102000	1.946676000	2.193210000
1	1.396386000	1.915181000	1.396546000
1	1.603944000	0.433782000	-0.847700000
1	-3.828084000	0.754570000	0.379847000
1	-3.657870000	-0.307629000	-2.100081000
1	-1.061066000	-0.704966000	-2.710036000