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Effect of a single methyl substituent on the electronic structure of cobaltocene studied by computationally assisted MATI spectroscopy

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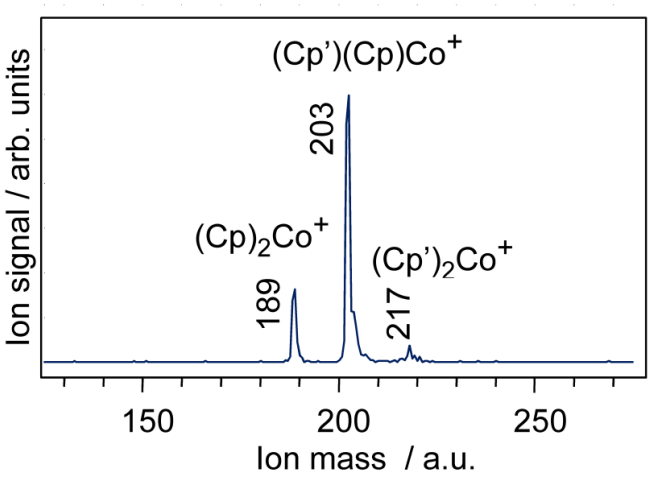

Figure S1. Photoionization mass-spectrum of the $(Cp)_2Co$ / (Cp')(Cp)Co / $(Cp')_2Co$ mixture synthesized.

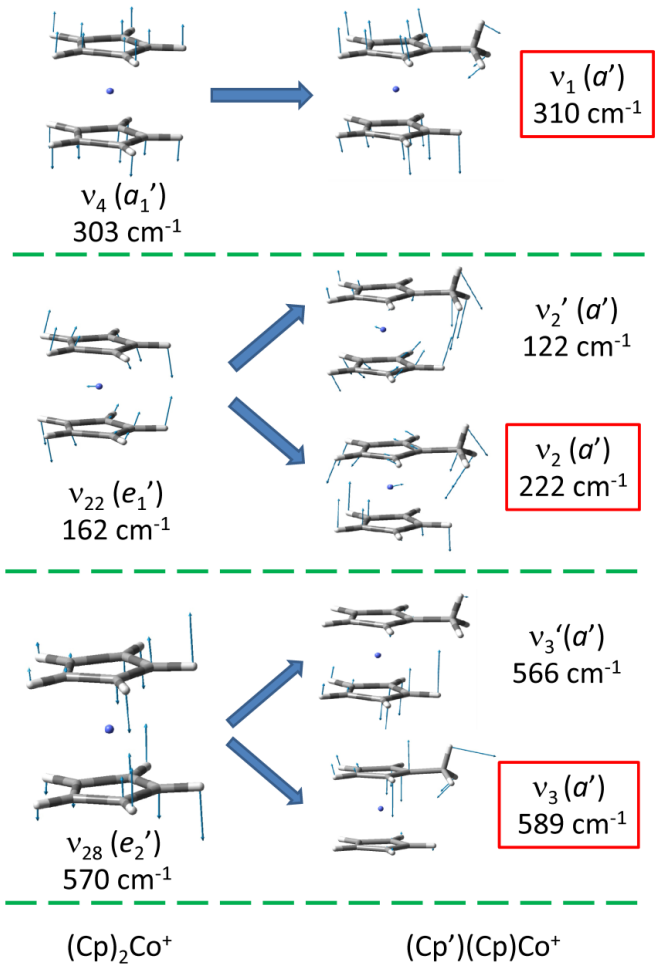

Figure S2. Relative atomic shifts and calculated (BPW91/TZVP) frequencies of the $(Cp)_2Co^+$ vibrations revealed by the MATI spectrum[1] and the corresponding (Cp')(Cp)Co^+ modes. Only those components of the $(Cp)_2Co^+$ e_2' modes that become totally symmetric on the JT symmetry reduction of the neutral molecule are shown. The (Cp')(Cp)Co^+ vibrations observed in the MATI spectrum measured in this work are indicated by red frames.

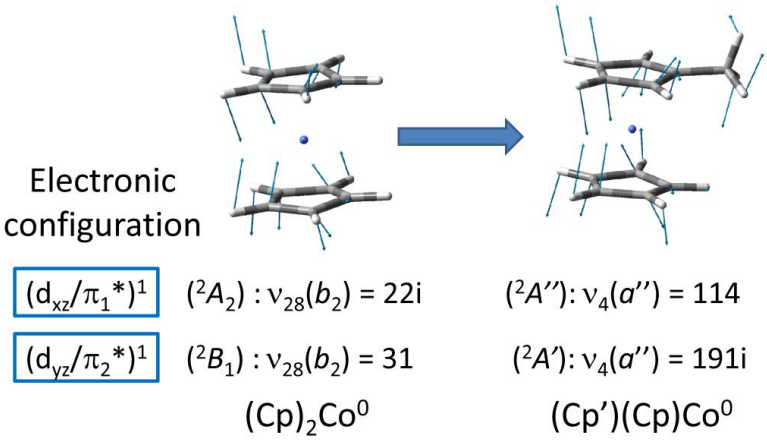

Figure S3. Relative atomic shifts and calculated (BPW91/TZVP) frequencies of the b_2 component of the ν_{28} mode in $(Cp)_2Co^0$ and the corresponding $\nu_4(a'')$ vibration in $(Cp')(Cp)Co^0$. The frequencies are given for the $[d_{xz},\pi_1^*]^1$ and $[d_{yz},\pi_2^*]^1$ electronic configurations. The symmetries of the electronic states are indicated.

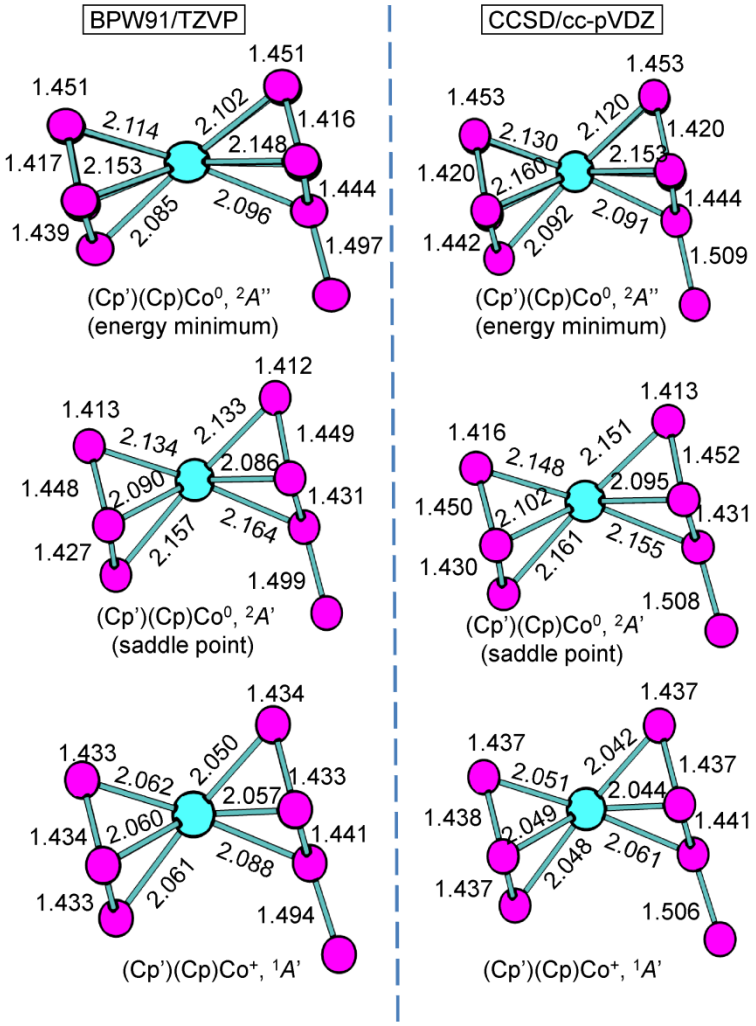

Figure S4. Co-C and C-C bond lengths in the DFT and CCSD optimised A'' and A' states of the $(Cp')(Cp)Co^0$ neutral and the closed-shell $(Cp')(Cp)Co^+$ ion.

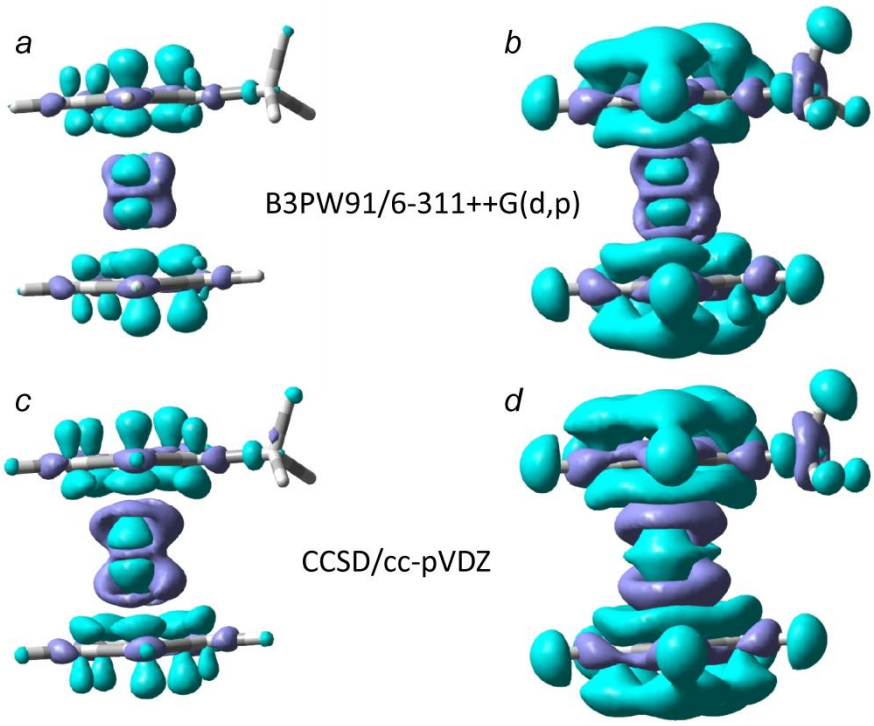

Figure S5. B3PW91/6-311++G(d,p) (a, b) and CCSD/cc-pVDZ (c, d) electron density difference isosurfaces at 0.005 a.u. (a, c) and 0.002 a.u. (b, d) corresponding to ionization of (Cp')(Cp)Co^0. The violet and blue colours indicate the positive and negative EDD values, respectively.

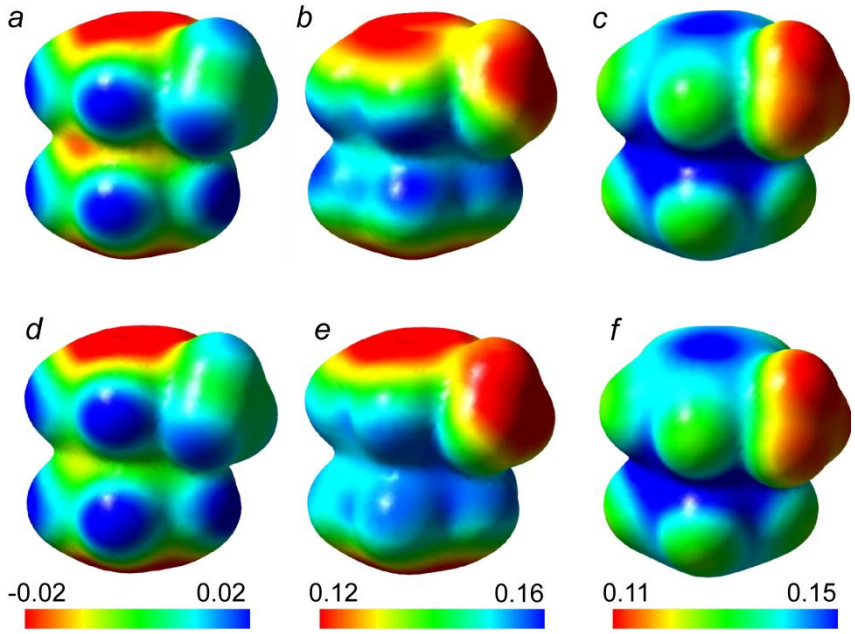

Figure S6. B3PW91/6-311++G(d,p) (a, b) and CCSD/cc-pVDZ (d, e) molecular electrostatic potential (MEP) mapped onto the ED isosurface (0.001 a.u.) of (Cp')(Co)Co^0 (a, d) and (Cp')(Cp)Co^+ (b, e) and the difference between the ion and neutral MEP at the optimised geometry of (Cp')(Co)Co^0 (c, f).

Table S1. Calculated ionization potentials based on the electronic energies I_{el} (eV), the differences between the ion and neutral zero-point energies ΔZPE (eV) and their sums calculated at various levels of theory for $(Cp)_2Co$ / (Cp')(Cp)Co.

Method	I_{el}	ΔZPE	I_{el} +ΔZPE
BPW91/TZVP	5.11 / 4.983	0.146 / 0.137	5.256 / 5.12
B3PW91/6-311+G(d,p)	5.412 / 5.286	0.145 / 0.139	5.557 / 5.425
B3PW91/6-311+G(d,p), D3	5.368 / 5.244	0.146 / 0.139	5.515 / 5.383
B3PW91/6-311++G(d,p)	5.41 / 5.287	0.145 / 0.139	5.556 / 5.426
B3LYP/6-311++G(d,p)	5.503 / 5.379	0.144 / 0.137	5.647 / 5.517
CCSD/cc-pVDZ	5.309 / 5.192	—	5.446 / 5.329
CCSD/cc-pVTZ	5.47 / 5.084	—	5.616 / 5.221
CCSD(T)/cc-pVDZ	5.027 / 4.915	—	5.173 / 5.052
CCSD(T)/cc-pVTZ	5.196 / 5.084	—	5.342 / 5.221

Table S2. Calculated and experimental frequencies (cm^{-1}) of the ν_1 - ν_3 vibrations in the (Cp')(Cp)Co^+ cation.

Method	ν_1	ν_2	ν_3
BPW91/TZVP	310	589	222
B3PW91/6-311+G(d,p)	323	596	230
B3PW91/6-311+G(d,p), D3	332	602	230
B3PW91/6-311++G(d,p)	323	596	231
TPSSh/6-311+G(d,p)	326	592	229
B3LYP/6-311++G(d,p)	310	589	225
MATI experiment	312	585	219

Table S3. Selected interatomic distances (Å) in the (Cp')(Cp)Co^0 structures corresponding to the the $^2A''$ and $^2A'$ PES cross-section minima[a] (Figure 4 see the main text) and averaged geometry[b] as well as distances in the closed-shell (Cp')(Cp)Co^+ cation. The distances are calculated at the BPW91/B3PW91/CCSD levels of theory.

Atoms	$^2A''$	$^2A'$	Averaged geometry	(Cp')(Cp)Co^+
Co20-C4	2.096/2.090/2.091	2.164/2.153/2.155	2.130/2.121/2.123	2.088/2.067/2.061
Co20-C5	2.148/2.141/2.153	2.086/2.082/2.095	2.117/2.112/2.124	2.057/2.040/2.044
Co20-C7	2.102/2.101/2.120	2.133/2.132/2.152	2.117/2.117/2.136	2.050/2.035/2.043
Co20-C12	2.085/2.079/2.092	2.157/2.148/2.161	2.121/2.113/2.126	2.061/2.043/2.048
Co20-C10	2.153/2.146/2.160	2.090/2.087/2.102	2.122/2.116/2.131	2.060/2.043/2.049
Co20-C17	2.114/2.112/2.130	2.134/2.132/2.148	2.124/2.122/2.139	2.062/2.045/2.051
C4-C5	1.444/1.433/1.444	1.431/1.421/1.431	1.436/1.426/1.436	1.441/1.430/1.441
C5-C7	1.416/1.408/1.420	1.449/1.439/1.452	1.432/1.423/1.435	1.433/1.424/1.437
C1-C7	1.451/1.440/1.453	1.412/1.402/1.413	1.431/1.421/1.433	1.434/1.424/1.437
C10-C12	1.439/1.429/1.442	1.427/1.418/1.430	1.431/1.422/1.434	1.433/1.424/1.437
C10-C17	1.417/1.408/1.420	1.448/1.437/1.450	1.432/1.422/1.434	1.434/1.425/1.438
C15-C17	1.451/1.441/1.453	1.413/1.404/1.416	1.432/1.422/1.434	1.433/1.424/1.437

[a]The $^2A'$ PES cross-section minimum actually represents a saddle point on the three-dimensional PES;
[b] – the coordinates of each atom in the 2A'' and 2A' optimized structures are averaged.

Table S4. BPW91/TZVP and CCSD/cc-pVDZ atom and fragment QTAIM charges (a.u.) in (Cp')(Cp)Co^0 and (Cp')(Cp)Co^+ and their difference Δq.

Atom or fragment	(Cp')(Cp)Co^0		(Cp')(Cp)Co^+		Δq	
	BPW91/ TZVP	CCSD/ cc-pVDZ	BPW91/ TZVP	CCSD/ cc-pVDZ	BPW91/ TZVP	CCSD/ cc-pVDZ
C1	-0.122	-0.098	-0.084	-0.079	0.037	0.019
C2	-0.110	-0.073	-0.094	-0.093	0.016	-0.019
H3	0.044	-0.025	0.103	0.055	0.060	0.080
C4	-0.101	-0.158	-0.058	-0.116	0.043	0.042
C5	-0.110	-0.073	-0.094	-0.093	0.015	-0.019
H6	0.044	-0.025	0.103	0.055	0.060	0.080
C7	-0.122	-0.098	-0.084	-0.079	0.037	0.019
H8	0.048	-0.022	0.109	0.066	0.062	0.088
H9	0.048	-0.022	0.109	0.066	0.062	0.088
C10	-0.104	-0.062	-0.085	-0.078	0.019	-0.016
H11	0.047	-0.017	0.108	0.066	0.061	0.083
C12	-0.136	-0.122	-0.085	-0.079	0.051	0.043
C13	-0.103	-0.062	-0.085	-0.078	0.018	-0.016
H14	0.047	-0.017	0.108	0.066	0.061	0.083
C15	-0.122	-0.096	-0.084	-0.078	0.038	0.018
H16	0.047	-0.021	0.109	0.067	0.062	0.088
C17	-0.122	-0.096	-0.084	-0.078	0.038	0.018
H18	0.047	-0.021	0.109	0.067	0.062	0.088
H19	0.046	-0.027	0.107	0.064	0.061	0.091
Co20	0.672	1.073	0.695	1.081	0.023	0.008
C21	0.004	0.285	0.000	0.276	-0.004	-0.009
H22	0.018	-0.077	0.050	-0.038	0.032	0.039
H23	0.021	-0.068	0.073	-0.004	0.052	0.064
H24	0.018	-0.077	0.050	-0.038	0.032	0.039
Σq(C)	-1.146	-0.654	-0.837	-0.575	0.309	0.079
Σq(H)	0.474	-0.420	1.140	0.491	0.667	0.911
Cp	-0.351	-0.543	0.120	-0.062	0.472	0.481
Cp'	-0.321	-0.532	0.182	-0.022	0.504	0.510
Me	0.060	0.063	0.173	0.195	0.113	0.132

Table S5. Atomic coordinates (Å) in the DFT and CCSD optimized and averaged structures of methylcobaltocene (the .xyz file format).

24
(Cp')(Cp)Co^0, A'', BPW91/TZVP
C 0.725500 1.710700 -0.955300
C 1.166700 1.746100 0.390100
H 2.197300 1.739600 0.731900
C -0.000000 1.678700 1.237600
C -1.166700 1.746100 0.390100
H -2.197300 1.739600 0.731900
C -0.725500 1.710700 -0.955300
H -1.356700 1.698800 -1.838900
H 1.356700 1.698800 -1.838900
C -0.000000 1.735300 2.736600
H 0.889200 1.249800 3.158500
H -0.000000 2.781900 3.080900
H -0.889200 1.249800 3.158500
C -1.170200 -1.789400 0.343000
H -2.200500 -1.790600 0.683400
C -0.000000 -1.736600 1.178100
C 1.170200 -1.789400 0.343000
H 2.200500 -1.790600 0.683400
C 0.725300 -1.728200 -1.001200
H 1.355000 -1.701900 -1.885400
C -0.725300 -1.728200 -1.001200
H -1.355000 -1.701900 -1.885400
H -0.000000 -1.738200 2.264600
Co -0.000000 -0.014800 0.001900
24
(Cp')(Cp)Co^0, A', BPW91/TZVP
C 0.705800 1.731700 -0.962400
C 1.141400 1.657200 0.417500
H 2.177000 1.634100 0.747200
C -0.000000 1.705100 1.279100
C -1.141400 1.657200 0.417500
H -2.177000 1.634000 0.747200
C -0.705800 1.731800 -0.962400
H -1.353300 1.737700 -1.833500
H 1.353300 1.737600 -1.833500
C -1.145800 -1.753600 0.330300
H -2.181000 -1.746300 0.659300
C -0.000000 -1.842500 1.176600
C 1.145800 -1.753700 0.330300
H 2.181000 -1.746300 0.659300
C 0.706500 -1.758800 -1.049300
H 1.352600 -1.728200 -1.920900
C -0.706500 -1.758800 -1.049300
H -1.352600 -1.728200 -1.920900
H -0.000000 -1.871500 2.261100
Co -0.000000 -0.037700 -0.003900
C -0.000000 1.766700 2.776800
H 0.887700 1.277300 3.199400

H -0.000000 2.809900 3.132300
H -0.887700 1.277300 3.199400
24
(Cp')(Cp)Co^0, the averaged geometry, BPW91/TZVP
C 1.107300 -1.663200 0.715600
C 1.557900 -0.377000 1.154000
H 1.659500 -0.056600 2.187200
C 1.842800 0.428700 0.000000
C 1.557900 -0.377000 -1.154000
H 1.659500 -0.056700 -2.187200
C 1.107300 -1.663200 -0.715600
H 0.802500 -2.485900 -1.355000
H 0.802500 -2.485900 1.355000
C 2.413900 1.815200 -0.000000
H 2.101600 2.379400 0.888500
H 3.515400 1.784100 -0.000000
H 2.101600 2.379400 -0.888500
C -1.726300 0.755200 -1.158000
H -1.608200 1.068400 -2.190700
C -1.453900 1.550800 -0.000000
C -1.726300 0.755200 1.158000
H -1.608200 1.068500 2.190700
C -2.168700 -0.533100 0.715900
H -2.444100 -1.367200 1.353800
C -2.168700 -0.533100 -0.715900
H -2.444100 -1.367200 -1.353800
H -1.094700 2.575200 -0.000000
Co -0.203800 -0.162500 0.000000
24
(Cp')(Cp)Co^+, BPW91/TZVP
C 0.721300 1.638800 -0.956100
C 1.159100 1.623400 0.408200
H 2.192200 1.596400 0.742700
C 0.003500 1.632300 1.268300
C -1.151400 1.629500 0.407200
H -2.184900 1.608000 0.740900
C -0.712500 1.642600 -0.956700
H -1.351800 1.631800 -1.834200
H 1.361200 1.624600 -1.833100
C 0.003000 1.707000 2.760100
H 0.894700 1.240900 3.194800
H 0.005500 2.765200 3.064800
H -0.891400 1.245300 3.194000
C -1.164500 -1.691900 0.333700
H -2.197300 -1.679200 0.667800
C -0.005800 -1.717000 1.177000
C 1.154200 -1.698100 0.335300
H 2.186600 -1.690900 0.671000
C 0.712300 -1.665400 -1.029000
H 1.351400 -1.626900 -1.905600
C -0.720400 -1.661500 -1.030000
H -1.358100 -1.619700 -1.907500
H -0.006500 -1.727500 2.262500

Co -0.000400 -0.025800 -0.000800
24
(Cp')(Cp)Co^0, A'', CCSD/cc-PVDZ
C 1.640600 1.154600 0.726700
C 0.368500 1.604900 1.167300
H 0.036700 1.699500 2.203200
C -0.459100 1.799800 0.000000
C 0.368500 1.604900 -1.167300
H 0.036700 1.699500 -2.203200
C 1.640600 1.154600 -0.726700
H 2.481000 0.866700 -1.361300
H 2.481000 0.866700 1.361300
C -1.882700 2.300400 0.000000
H -2.427100 1.950200 0.894500
H -1.904900 3.406500 0.000000
H -2.427100 1.950200 -0.894500
C -0.734100 -1.765000 -1.171200
H -1.055800 -1.648100 -2.207400
C -1.507900 -1.437100 0.000000
C -0.734100 -1.765000 1.171200
H -1.055800 -1.648100 2.207400
C 0.555700 -2.158400 0.726400
H 1.402400 -2.430700 1.359600
C 0.555700 -2.158400 -0.726400
H 1.402400 -2.430700 -1.359600
H -2.539600 -1.077800 0.000000
Co 0.174100 -0.193200 0.000000
24
(Cp')(Cp)Co^0, A', CCSD/cc-PVDZ
C -1.726700 -1.083700 0.706700
C -0.415400 -1.528000 1.144600
H -0.098600 -1.632700 2.185200
C 0.367300 -1.882900 0.000000
C -0.415400 -1.528000 -1.144600
H -0.098600 -1.632700 -2.185200
C -1.726700 -1.083700 -0.706700
H -2.540800 -0.760200 -1.357800
H -2.540800 -0.760200 1.357800
C 1.760000 -2.462600 0.000000
H 2.323400 -2.139900 0.893500
H 1.730500 -3.568500 0.000000
H 2.323400 -2.139900 -0.893500
C 0.807300 1.678600 -1.149500
H 1.112300 1.550200 -2.190200
C 1.622000 1.433500 0.000000
C 0.807300 1.678600 1.149500
H 1.112300 1.550200 2.190200
C -0.467400 2.211200 0.707900
H -1.290000 2.515800 1.357400
C -0.467400 2.211200 -0.707900
H -1.290000 2.515800 -1.357400
H 2.638700 1.037100 0.000000
Co -0.157400 0.207400 0.000000

24
(Cp')(Cp)Co^{0}, the averaged geometry, CCSD/cc-PVDZ
C -1.663900 -1.149400 0.716700
C -0.364800 -1.573300 1.155900
H -0.038700 -1.667300 2.194200
C 0.446400 -1.834200 0.000000
C -0.364800 -1.573300 -1.155900
H -0.038700 -1.667300 -2.194200
C -1.663900 -1.149400 -0.716700
H -2.496600 -0.858200 -1.359600
H -2.496600 -0.858200 1.359600
C 1.864400 -2.349600 0.000000
H 2.412400 -2.003300 0.894000
H 1.880300 -3.455700 0.000000
H 2.412400 -2.003300 -0.894000
C 0.740700 1.735500 -1.160400
H 1.056300 1.618400 -2.198800
C 1.539100 1.463600 0.000000
C 0.740700 1.735500 1.160400
H 1.056300 1.618400 2.198800
C -0.550500 2.175900 0.717200
H -1.390300 2.449600 1.358500
C -0.550500 2.175900 -0.717200
H -1.390300 2.449600 -1.358500
H 2.570000 1.103800 0.000000
Co -0.169400 0.197400 0.000000
24
(Cp')(Cp)Co^{+}, CCSD/cc-PVDZ
C 0.930800 -1.697300 0.718500
C 1.456300 -0.433900 1.157700
H 1.561400 -0.111900 2.196000
C 1.789300 0.357300 -0.000000
C 1.456300 -0.433900 -1.157700
H 1.561400 -0.111900 -2.196000
C 0.930800 -1.697300 -0.718500
H 0.565800 -2.500300 -1.361600
H 0.565800 -2.500300 1.361600
C -1.581300 0.817400 -1.162600
H -1.430100 1.119000 -2.200800
C -1.256900 1.598000 -0.000300
C -1.581000 0.817900 1.162400
H -1.429700 1.120000 2.200400
C -2.105900 -0.444900 0.718500
H -2.421600 -1.269200 1.360600
C -2.106000 -0.445200 -0.718100
H -2.421900 -1.269900 -1.359700
H -0.814700 2.596200 -0.000600
Co -0.205800 -0.159200 -0.000000
C 2.411300 1.728800 -0.000000
H 2.122400 2.299200 0.898200
H 3.511500 1.627100 0.000100
H 2.122600 2.299200 -0.898300

References

1. S. Y. Ketkov and H. L. Selzle, *Angew. Chem. Int. Ed.*, 2012, **51**, 11527–11530.