

**Bis(cobaltocenium) tetrachlorocobaltate(II) dichloromethane solvate**

**Supplementary Material**

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**Table S1.** Dihedral Angles

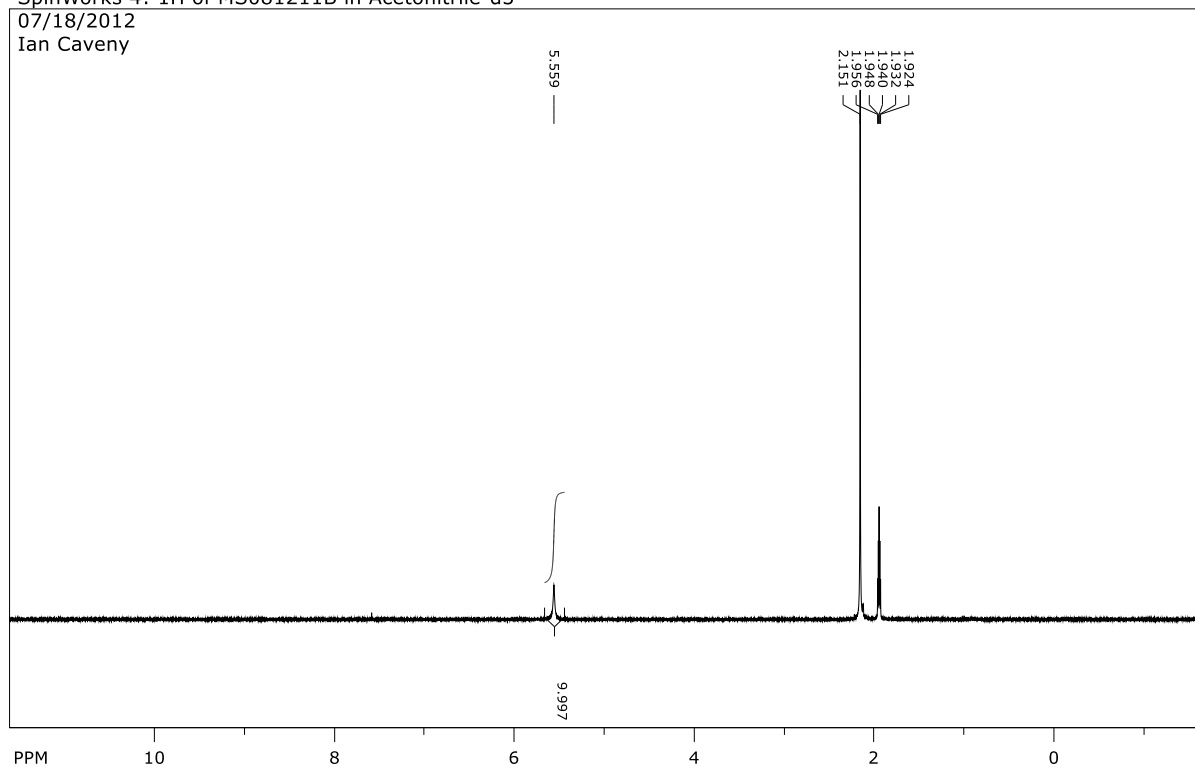
<b>Cobaltocenium unit label</b>	<b>Eclipse angle Dihedral Angle btw planes Centroid-Co-C1 Centroid-Co-C6</b>	<b>Coplanarity: Dihedral angle btw least-squares planes of Cp groups</b>
	degrees	degrees
<b>A</b>	3.09 (9)	1.21 (1)
<b>B</b>	1.49 (9)	1.47 (1)
<b>C</b>	5.50 (9)	0.99 (1)
<b>D</b>	0.65 (9)	2.35 (1)
<b>E</b>	2.02 (9)	0.99 (1)
<b>F</b>	3.02 (9)	0.81 (1)
<b>G</b>	3.69 (9)	3.47 (1)
<b>H</b>	2.20 (9)	1.34 (1)
<b>I</b>	1.75 (9)	2.46 (1)
<b>J</b>	6.30 (9)	1.17 (1)
<b>average</b>	<b>2.97 (9)</b>	<b>1.63 (1)</b>
<b>st dev</b>	<b>1.78</b>	<b>0.86</b>
<b>median</b>	<b>2.61 (9)</b>	<b>1.27 (1)</b>

**Note:** The  $R^2$  values for the least squares planes found for each cyclopentadienyl group were all greater than 0.9998.

SpinWorks 4: 1H of MS081211B in Acetonitrile-d3

07/18/2012

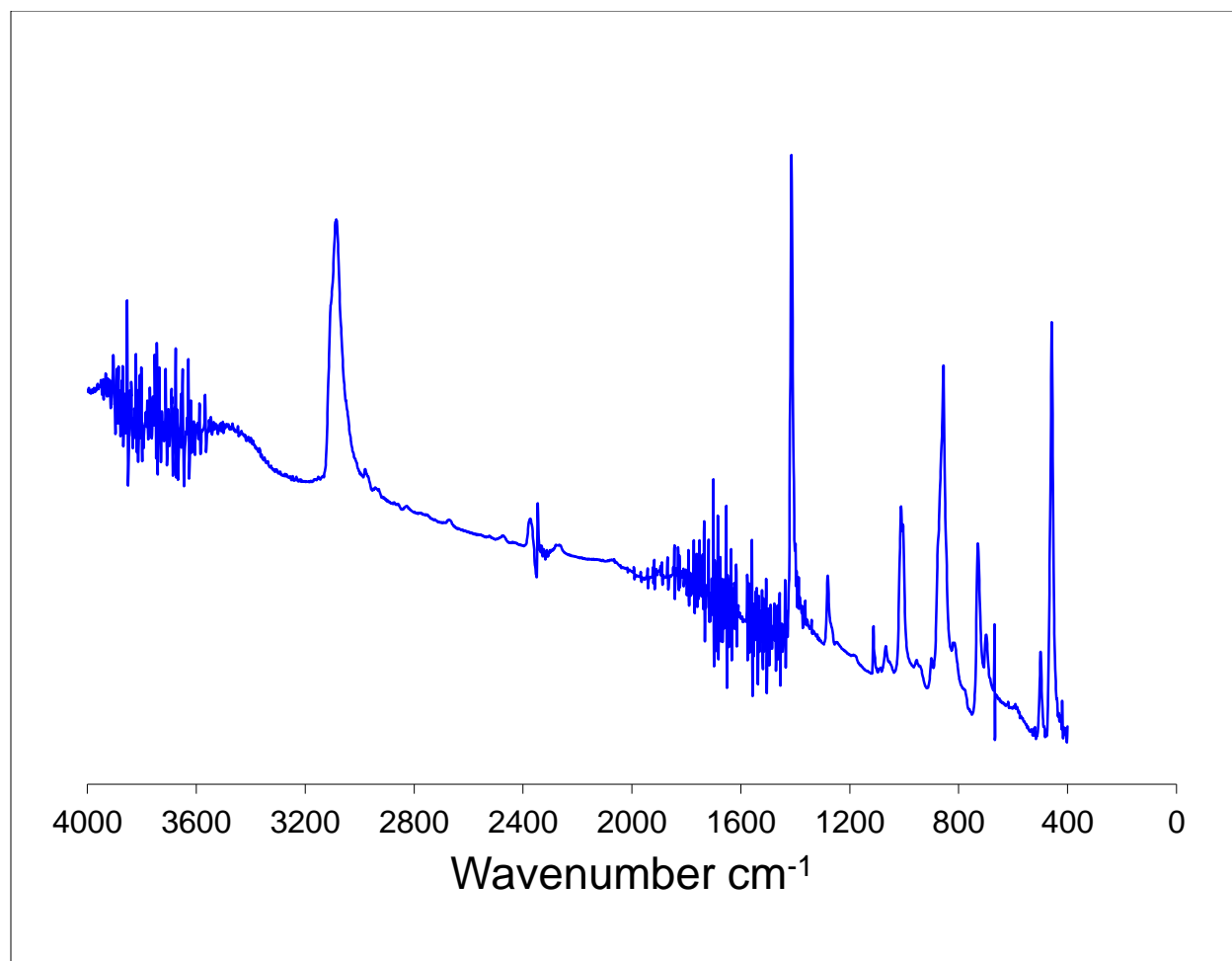
Ian Caveny



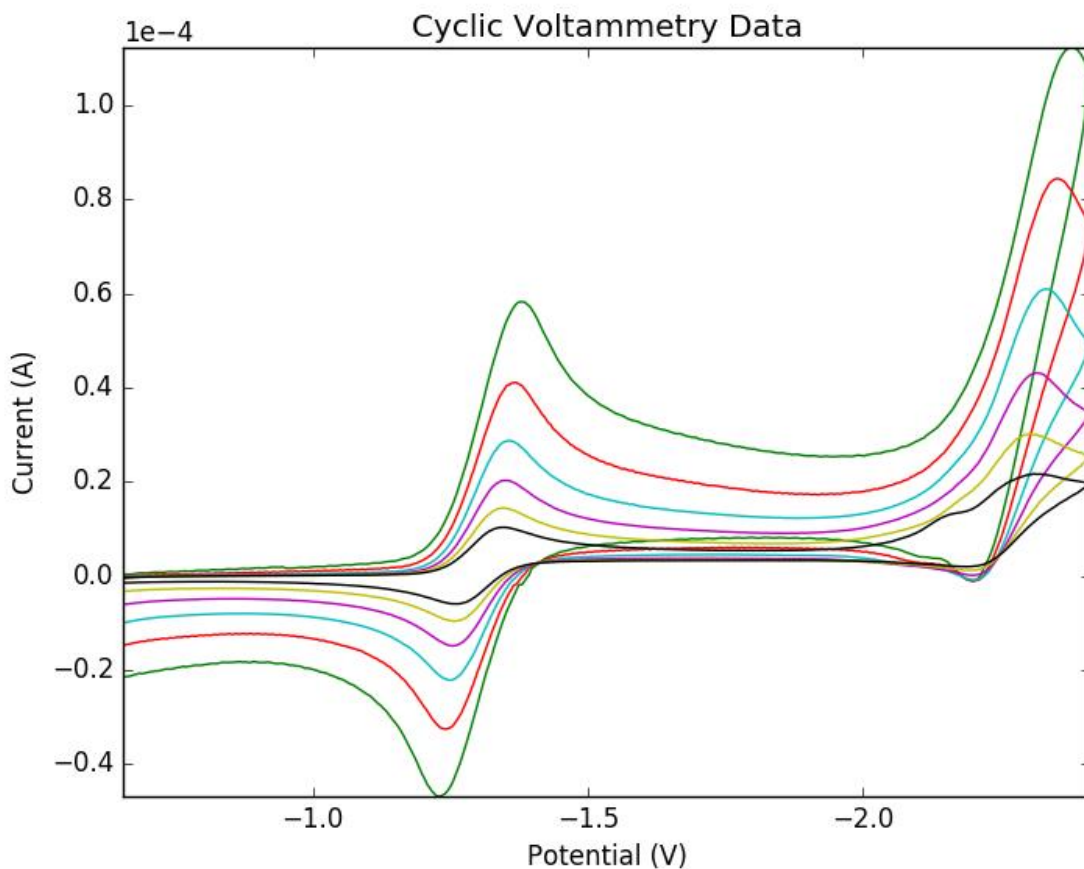
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time domain size: 29952 points  
width: 4000.00 Hz = 13.3311 ppm = 0.133547 Hz/pt  
number of scans: 16

freq. of 0 ppm: 300.049426 MHz  
processed size: 32768 complex points  
LB: 0.100 GF: 0.0000

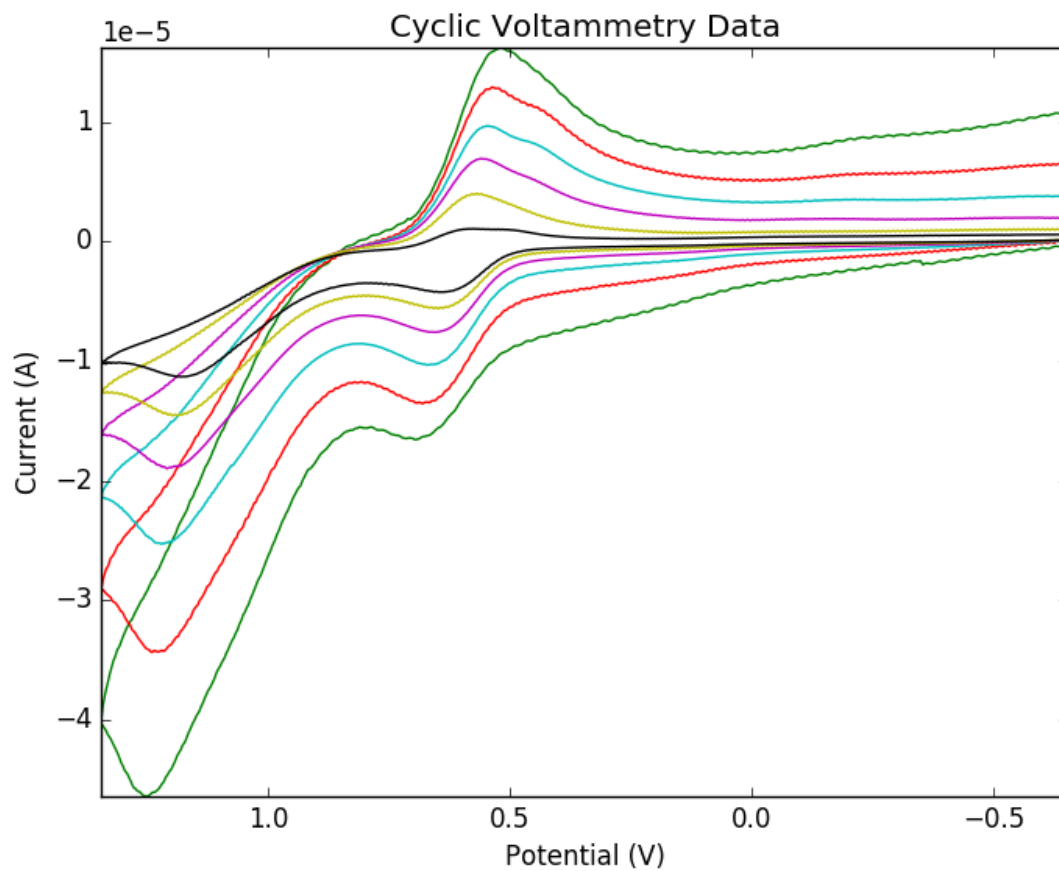
**Figure S1.** 300 MHz  $^1\text{H}$  NMR spectrum of  $[\text{Cp}_2\text{Co}][\text{CoCl}_4]$  dichloromethane solvate in  $\text{MeCN-}d^3$  at 298K. Peak assignments:  $\text{H}_2\text{O}$  at 2.15 ppm,  $\text{MeCN-}d^2$  at 1.94 ppm,  $[\text{Cp}_2\text{Co}]^+$  at 5.56 ppm.



**Figure S2.** Raman Spectrum of a crystal of  $5[\text{Cp}_2\text{Co}][\text{CoCl}_4] \cdot 6\text{CH}_2\text{Cl}_2$  obtained with 768 nm excitation.



**Figure S3.** CV data for reductions of 1.0 mM  $\{5[\text{Cp}_2\text{Co}]_2[\text{CoCl}_4] \cdot 6\text{CH}_2\text{Cl}_2\}$  in 0.1M  $\text{NBu}_4\text{PF}_6/\text{CH}_2\text{Cl}_2$  at 298K.  $\text{Cp}_2\text{Co}^{+/0}$  wave at -1.32 V vs  $\text{Cp}_2\text{Fe}^{+/0}$ . Features are consistent with the two known reductions of  $\text{Cp}_2\text{Co}^+$ . Scan rates: 0.05 V/s (black), 0.10 V/s (gold), 0.20 V/s (purple), 0.40 V/s (cyan), 0.80 V/s (red), 1.6 V/s (green).



**Figure S4.** CV data for oxidations of 1.0 mM  $\{5[\text{Cp}_2\text{Co}]_2[\text{CoCl}_4] \cdot 6\text{CH}_2\text{Cl}_2\}$  in 0.1M  $\text{NBu}_4\text{PF}_6/\text{CH}_2\text{Cl}_2$  at 298K.  $\text{Cp}_2\text{Co}^{+/0}$  wave at -1.32 V vs  $\text{Cp}_2\text{Fe}^{+/0}$ . Feature at +0.59 V vs  $\text{Cp}_2\text{Fe}^{+/0}$  consistent with oxidation of  $[\text{CoCl}_4]^-$ , displays chemical reversibility at faster scan rates. Scan rates: 0.05 V/s (black), 0.10 V/s (gold), 0.20 V/s (purple), 0.40 V/s (cyan), 0.80 V/s (red), 1.6 V/s (green).

## Refinement

A green, prism-shaped crystal of dimensions 0.26 x 0.28 x 0.44 mm was selected for structural analysis. Intensity data for this compound were collected using a diffractometer with a Bruker APEX ccd area detector [Bruker, 2007*a* & 2007*b*] and graphite-monochromated Mo K $\alpha$  radiation ( $\lambda = 0.71073 \text{ \AA}$ ). The sample was cooled to 100(2) K. Cell parameters were determined from a least-squares fit of 8748 peaks in the range  $2.28 < \theta < 28.29^\circ$ . A total of 74645 data were measured in the range  $1.298 < \theta < 28.301^\circ$  using  $\omega$  oscillation frames. The data were corrected for absorption by the empirical method [Krause et al, 2015] giving minimum and maximum transmission factors of 0.396 and 0.553. The data were merged to form a set of 31791 independent data with  $R(\text{int}) = 0.0443$  and a coverage of 99.9 %.

The triclinic space group  $P\bar{1}$  was determined by statistical tests and verified by subsequent refinement. The structure was solved by direct methods and refined by full-matrix least-squares methods on  $F^2$  [Sheldrick 2015*a*, 2015*b*]. The positions of hydrogens were initially determined by geometry and were refined using a riding model. Non-hydrogen atoms were refined with anisotropic displacement parameters. Hydrogen atom displacement parameters were set to 1.2 times the isotropic equivalent displacement parameters of the bonded atoms. A total of 1378 parameters were refined against 31791 data to give  $wR(F^2) = 0.0912$  and  $S = 0.990$  for weights of  $w = 1/[\sigma^2(F^2) + (0.0340 P)^2 + 0.9300 P]$ , where  $P = [F_o^2 + 2F_c^2] / 3$ . The final  $R(F)$  was 0.0429 for the 23455 observed,  $[F > 4\sigma(F)]$ , data. The largest shift/s.u. was 0.002 in the final refinement cycle. The final difference map had maxima and minima of 0.622 and -0.511 e/ $\text{\AA}^3$ , respectively.

## References

Bruker (2007*a*). *APEX2*. Bruker AXS Inc., Madison, Wisconsin, USA.

Bruker (2007*b*). *SAINT*. Bruker AXS Inc., Madison, Wisconsin, USA.

Krause, L., Herbst-Irmer, R., Sheldrick, G. M. & Stalke, D. (2015). *J. Appl. Cryst.* **48**, 3-10.

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