# HFEPR of a Long-Ignored High-Spin Metallocene: Chromocenium

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## Introduction

Metallocenes, i.e., complexes of the ligand cyclopenta-1,4-dienide anion, $C_5H_5^-$, $Cp^-$, have been known for over 60 years. Metallocenes are important as reagents and catalysts in many organic synthesis and polymerization processes. They have recently been investigated for use as anti-cancer agents.

Our interest is in the electronic structure of paramagnetic metallocenes, in particular those with $S > 1/2$. In general, higher symmetry is required to achieve the orbital degeneracy that yields multiple unpaired electrons. Therefore, we have been focusing on homoleptic, biscyclopentadienide complexes, $[MCp_2]^{n+}$.

The first of these to be studied was vanadocene, $[VCp_2]$, which contains a V(II) ($3d^3$, $S = 3/2$) ion. The complex yields conventional EPR, but the definitive determination of its zero-field splitting (zfs) parameters required HFEPR.[1] There is also the Cr(III) congener, chromocenium, $[CrCp_2]^+$, which was first reported over 50 years ago by (later) Nobel Laureate E. O. Fisher.[2] Their magnetic studies suggested an $S = 3/2$ ground state, as with vanadocene. X-band EPR spectra of $[VCp_2]$ and $[CrCp_2]^+$ (which have never been reported, to our knowledge) are similar. Moreover, no crystal structure of chromocenium has been reported. Synthetic advances since Fischer's time can also be taken advantage of, namely use of the very weakly coordinating anion, $[B\{3,5\text{-}(CF_3)_2C_6H_3\}_4]^-$, abbreviated as $[BAr^F{}_4]^-$.

## Experimental

[CrCp2][$BAr^F{}_4$] was prepared using a modification of Fischer and Ulm's original procedure, and will be described elsewhere. X-ray crystallographic studies on this complex will also be performed.

The EMR Facility and the 17-T SC magnet at NHMFL were used to measure HFEPR spectra of powder and frozen solution (toluene/dichloromethane 1:1) samples of $[CrCp_2][BAr^F{}_4]$.

## Results and Discussion

Figure 1 presents a HFEPR spectrum of $[CrCp_2][BAr^F{}_4]$ in solution. Some decomposition, likely to Cr(V) ($3d^1$, $S = 1/2$) has occurred (confirmed by X-band EPR; not shown), but there are clearly identifiable, very narrow signals, due to the compound of interest. Note that in contrast to V, ($^{51}V$, $I = 7/2$, 100%), the sole magnetic isotope of Cr is of low abundance ($^{53}Cr$, $I = 3/2$, 9.5%), affording narrower lines but no hyperfine information. The signals, as with $[VCp_2]$, are perfectly axial ($E = 0$), indicating the linear ($C_5$ symmetry) geometry. The $D$ value is close to that for $[VCp_2]$ as well.

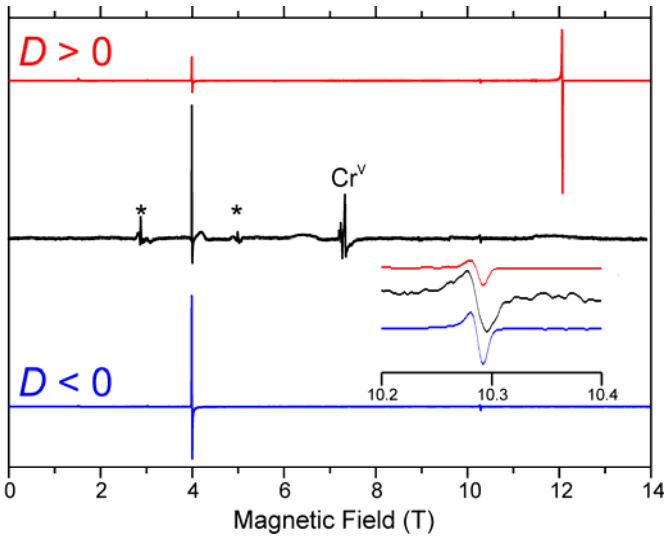


**Figure 1.** HFEPR of $[CrCp_2][BAr^F{}_4]$ in toluene/DCM at 203.2 GHz, 5 K (black trace). Simulations use $S = 3/2$, $|D| = 4.80$ $cm^{-1}$, $E = 0$, $g = 2.00$, with sign of zfs as indicated, showing the better correspondence with $D < 0$. Inset shows an expansion of the spectral feature at 10.3 T. (* = $O_{2(s)}$ signals).

## Conclusions

HFEPR is able to conclusively document the spin quartet ground state of this long known, but apparently forgotten, Cr(III) metallocene. Computational analysis by *ab initio* methods will be made, as done previously for vanadocene.[1]

## Acknowledgements

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## References

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[2] Fischer, E. O. and Ulm, K., Chem. Ber. **95**, 692–694 (1962).