Coexistence of metallocene cations and anions

Created by Chip Nataro, Lafayette College (nataroc@lafayette.edu) and posted on VIPEr (www.ionicviper.org) on September 23, 2025,

This paper presents a complex salt in which both the cation and anion are metallocenes (*J. Am. Chem. Soc.* ***2025****, 147,* 34641-34646 https://doi.org/10.1021/jacs.5c09718). It is a relatively short paper but provides many avenues for inquiry and further reading. This literature discussion will only touch on some of the various methods presented in this work. This discussion is somewhat unusual for this author in that students should answer the first two questions PRIOR to actually reading the paper.

1) A recent report (*J. Am. Chem. Soc.* ***2025****, 147,* 34641-34646) presents a unique ionic complex in which both the cation and the anion are organometallic compounds. The ions have similar formula, $[Rh(C_5Me_5)(C_5(CF_3)_5]$ and $[Co(C_5Me_5)_2]$ and a charge of ±1 so that the formula for the complex contains one cobalt and one rhodium. Using your chemical intuition, which ion is likely to be the cation and which is the anion? Why?

2) Both ions are 18-electron species. Using the Covalent Bond Classification system, determine the valence number, electron count, ligand bond number and d^n count for the metal centers in the cation and anion. If one of your ions does not have an electron count of 18, suggest how you might reach a count of 18.

3) Briefly summarize some of the reasons metallocenes are of interest.

4) Summarize in your own words the point the authors are making starting at "As harsh reductive conditions…" in the second paragraph through the end of the paragraph.

5) Figure 1 presents the reduction potentials for several different metallocene compounds. The key in that figure uses colors to show the different metal valences for each redox event. Consider ferrocene, $[(C_5H_5)_2Fe]$, which has a potential of 0.0 V. Write a half-reaction for the process taking place clearly indicating how the metal valence and electron count change during this process. As a reminder, reduction potentials are set against a standard. For aqueous systems, the standard hydrogen electrode is chosen as the reference of 0.0V and all other half-reactions are set relative to this. For organometallic compounds in non-aqueous solvents, ferrocene is a common reference and the potential is set at 0.0 V with other compounds being set relative to that.

6) Again, from Figure 1, compare the reduction potentials for $[Fe(C_5Me_5)_2]$, $[Fe(C_5H_5)_2]$ and $[Fe(C_5H_5)(C_5(CF_3)_5]$. All three compounds undergo a one-electron redox process. The potential for a redox process is directly proportional to the Gibb's Free Energy of the process through the equation $\Delta G = -nFE$ where n is the number of electrons and F is Faraday's constant (96,485 Coulomb/mol). Using the potential (E) in volts, gives the ΔG in Joules. Which compound is the easiest to oxidize? The hardest? How can you rationalize your choices?

Coexistence of metallocene cations and anions

7) Compare the potentials for the two different (orange and red) redox processes for $[Fe(C_5Me_5)_2]$. Based on your answer to the previous question, rationalize the relative potentials at which these two processes occur.

8) From Figure 1, do methyl groups or trifluoromethyl (CF_3) groups seem to have a bigger impact on reduction potential? Describe how you reached this conclusion.

9) Figure 2A presents the synthesis of $[Rh(C_5Me_5)(C_5(CF_3)_5][BF_4]$ ([**1**][BF_4]) which is essentially a metathesis reaction. In the first paragraph of the results and discussion, the authors suggest that the solvated, 12-electron fragment $[Rh(C_5Me_5)]^+$ initially forms. Why do the authors need to add $Ag[BF_4]$ to perform this reaction?

10) Figure 2B displays the reductive electrochemistry of [**1**][BF_4]. There are two waves in the cyclic voltammogram indicating two different reductive processes. The authors label the first wave as a Rh(II/III) couple in which [**1**]$^+$ is converted to [**1**]. Using the Covalent Bond Classification system, determine the valence number, electron count, ligand bond number and d^n count for [**1**][BF_4]. While the authors did not isolate the product of this initial reduction, they did attempt to characterize it using EPR (see the second paragraph in the left column of the third page of the paper). Using the Covalent Bond Classification system, determine the valence number, electron count, ligand bond number and d^n count for [**1**] and suggest why the authors would use EPR to characterize this compound. If you are unfamiliar with EPR, feel free to look it up, just be sure to cite your source.

11) The second wave in Figure 2B is labeled as the Rh(II/III) couple. This is due to the formation of [**1**]$^-$ the structure of which is presented in Figure 2C. If you did not come up with this sort of structure in question 2, use the Covalent Bond Classification system to determine the valence number, electron count, ligand bond number and d^n count for [**1**]$^-$.

12) In looking at the 'This work' box in Figure 1, suggest the significance of the reduction potentials to the two compounds that are shown with respect to the synthesis presented in Figure 2C. In other words, what process is going on in the synthesis in Figure 2C and why does it work? Would this reaction work with $[Co(C_5H_5)_2]$? Why or why not?

13) The supporting information presents the NMR data for the compounds presented in this study. While the ^1H and $^{13}C\{^1H\}$ spectra are reported, we will focus on the other nuclei. Compound [**1**][BF_4] displays three singlets in the ^{19}F NMR spectrum: -51.8, -152.5 and -152.6 ppm. The compound $[Co(C_5Me_5)_2]$[**1**] also displays three singlets in the ^{19}F NMR spectrum at -49.3, -53.3 and -58.1 ppm. Explain the ^{19}F spectra of these compounds.

Coexistence of metallocene cations and anions

Created by Chip Nataro, Lafayette College (nataroc@lafayette.edu) and posted on VIPEr (www.ionicviper.org) on September 23, 2025,

14) The ^{103}Rh spectrum for [**1**][BF_4] has a peak at -9308 ppm while [Co(C_5Me_5)$_2$][**1**] has a peak at -6895. This is a pretty significant difference. Suggest reason(s) why these two compounds might exhibit such different chemical shifts.

15) In [**1**]$^-$, why does the $C_5(CF_3)_5$ ring and not the C_5Me_5 ring slip?