Synthetic, Spectroscopic, Structural, and Electrochemical Investigations of Ferricenium Derivatives with Weakly Coordinating Anions: Ion Pairing, Substituent, and Solvent Effects

Firoz Shah Tuglak Khan,[§] Amy L. Waldbusser,[§] Maria C. Carrasco, Hadi Pourhadi, Shabnam Hematian*

Department of Chemistry and Biochemistry, University of North Carolina at Greensboro, Greensboro, NC 27402, USA

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1,1'-Dimethylferricenium $BArF_{20}$ ($^{Me2}FcBArF_{20}$)

n-Butylferricenium $BArF_{20}(^{nBu}\mathbf{Fc}BArF_{20})$

Ferricenium $BArF_{20}(FcBArF_{20})$

1-Bromoferricenium $BArF_{20}({}^{Br}\mathbf{Fc}BArF_{20})$

 $1\text{-}Acetylferricenium BArF_{20}({}^{Ac}\textbf{Fc}BArF_{20})$

 $1\text{-}Benzoyl ferricenium BArF_{20}({}^{\mathit{Bz}}\mathbf{Fc}BArF_{20})$

1,1'-Dibromoferricenium $BArF_{20}({}^{Br2}FcBArF_{20})$

1,1'-Diacetylferricenium $BArF_{20}$ ($^{Ac2}FcBArF_{20}$)

1,1'-Dibenzoylferricenium $SbF_6(^{Bz2}Fc[SbF_6])$

Tetra-*n*-butylammonium BArF₂₀ ($[(nBu)_4N][B(C_6F_5)_4]$)

 $Tetrakis(acetonitrile)silver(I) BArF_{20}([Ag(MeCN)_4][B(C_6F_5)_4])$

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1. Spectroscopic Data for Characterization of Various Compounds

NMR symbols for residual deuterated and protic solvents include the following: water (+), hexanes (^), acetone (*), dichloromethane (Δ), chloroform (‡), acetonitrile (ϕ).



Figure S1. IR spectra comparison between $K[B(C_6F_5)_4]$ (dotted line) and $[Ag(MeCN)_4][B(C_6F_5)_4]$ (solid line).



Figure S2. IR spectra comparison between $[Ag(CD_3CN)_4][B(C_6F_5)_4]$ (dotted line) and $[Ag(MeCN)_4][B(C_6F_5)_4]$ (solid line).



Figure S3. Cyclic voltammograms at 100 mV/s of 1 mM tris(4-bromophenyl)amine in DCM with 100 mM of either $[(nBu)_4N][B(C_6F_5)_4]$ (solid line, $E_{1/2} = 1.252$ V) or $[(nBu)_4N][PF_6]$ (dashed line, $E_{1/2} = 1.267$ V) as the supporting electrolyte. The potentials were collected vs a leak-free Ag/AgCl reference electrode. The working electrode was glassy carbon and the counter electrode was a carbon rod.



Figure S4. IR spectra comparison between ^{Me10}Fc (dotted line) and ^{Me10}FcBArF₂₀ (solid line).



Figure S5. IR spectra comparison between ^{Me2}Fc (dotted line) and ^{Me2}FcBArF₂₀ (solid line).



Figure S6. IR spectra comparison between nBu **Fc** (dotted line) and nBu **Fc**BArF₂₀ (solid line).



Figure S7. IR spectra comparison between Fc (dotted line) and $FcBArF_{20}$ (solid line).



Figure S8. IR spectra comparison between ^{Br}**Fc** (dotted line) and ^{Br}**Fc**BArF₂₀ (solid line).



Figure S9. IR spectra comparison between ${}^{Ac}\mathbf{Fc}$ (dotted line) and ${}^{Ac}\mathbf{Fc}BArF_{20}$ (solid line).



Figure S10. IR spectra comparison between Bz **Fc** (dotted line) and Bz **Fc**BArF₂₀ (solid line).



Figure S11. IR spectra comparison between Br_2 **Fc** (dotted line) and Br_2 **Fc**BArF₂₀ (solid line).



Figure S12. IR spectra comparison between ${}^{Ac2}Fc$ (dotted line) and ${}^{Ac2}FcBArF_{20}$ (solid line).



Figure S13. IR spectra comparison between Bz2 **Fc** (dotted line) and Bz2 **Fc**[SbF₆] (solid line).



Figure S14. ¹H-NMR spectrum of **Fc** recorded in acetone- d_6 (500 MHz) at room temperature.



Figure S15. ¹H-NMR spectrum of **Fc**BArF₂₀ recorded in acetone-*d*₆ (500 MHz) at room temperature.



Figure S16. ¹H-NMR spectrum of Me10 **Fc** recorded in acetone- d_6 (500 MHz) at room temperature.



Figure S17. ¹H-NMR spectrum of ^{*Me10*}**Fc**BArF₂₀ recorded in acetone-*d*₆ (500 MHz) at room temperature.



Figure S18. ¹H-NMR spectrum of Me2 **Fc** recorded in acetone- d_6 (500 MHz) at room temperature.



Figure S19. ¹H-NMR spectrum of ^{Me2}**Fc** recorded in CDCl₃ (500 MHz) at room temperature.



Figure S20. ¹H-NMR spectrum of nBu **Fc** recorded in acetone- d_6 (500 MHz) at room temperature.



Figure S21. ¹H-NMR spectrum of ^{*nBu*}Fc recorded in CDCl₃ (500 MHz) at room temperature.



Figure S22. ¹H-NMR spectrum of ^{*Br*}**Fc** recorded in acetone- d_6 (500 MHz) at room temperature.



Figure S23. ¹H-NMR spectrum of ^{*Ac*}**Fc** recorded in acetone- d_6 (500 MHz) at room temperature.



Figure S24. ¹H-NMR spectrum of ^{*Bz*}**Fc** recorded in acetone- d_6 (500 MHz) at room temperature.



Figure S25. ¹H-NMR spectrum of ^{Bz}**Fc** recorded in CDCl₃ (500 MHz) at room temperature.



Figure S26. ¹H-NMR spectrum of Br_2 **Fc** recorded in acetone- d_6 (400 MHz) at room temperature.



Figure S27. ¹H-NMR spectrum of ^{Br2}**Fc** recorded in CDCl₃ (500 MHz) at room temperature.



Figure S28. ¹H-NMR spectrum of Ac2 **Fc** recorded in acetone- d_6 (500 MHz) at room temperature.



Figure S29. ¹H-NMR spectrum of Bz2 **Fc** recorded in acetone- d_6 (500 MHz) at room temperature.



Figure S30. ¹H-NMR spectrum of ^{*Me2*}**Fc**BArF₂₀ recorded in acetone-*d*₆ (500 MHz) at room temperature.



Figure S31. ¹H-NMR spectrum of ^{*Me*2}**Fc**BArF₂₀ recorded in CD₂Cl₂ (500 MHz) at room temperature.



Figure S32. ¹H-NMR spectrum of ^{Br2}**Fc**BArF₂₀ recorded in acetone-*d*₆ (400 MHz) at room temperature.



Figure S33. ¹H-NMR spectrum of ^{Br2}**Fc**BArF₂₀ recorded in CD₂Cl₂ (500 MHz) at room temperature.



Figure S34. ¹H-NMR spectrum of ^{Ac2}**Fc**BArF₂₀ recorded in CD₂Cl₂ (500 MHz) at room temperature.



Figure S35. ¹H-NMR spectrum of Bz2 **Fc**[SbF₆] recorded in CD₂Cl₂ (500 MHz) at room temperature.



Figure S36. ¹H-NMR spectrum of nBu **Fc**BArF₂₀ recorded in acetone- d_6 (500 MHz) at room temperature.



Figure S37. ¹H-NMR spectrum of ^{*nBu*}**Fc**BArF₂₀ recorded in CD₂Cl₂ (500 MHz) at room temperature.



Figure S38. ¹H-NMR spectrum of ^B**Fc**BArF₂₀ recorded in acetone-*d*₆ (500 MHz) at room temperature.



Figure S39. ¹H-NMR spectrum of ^{*Br*}**Fc**BArF₂₀ recorded in CD₂Cl₂ (500 MHz) at room temperature.



Figure S40. ¹H-NMR spectrum of ^{Ac}**Fc**BArF₂₀ recorded in acetone-*d*₆ (500 MHz) at room temperature.



Figure S41. ¹H-NMR spectrum of ^{Ac}**Fc**BArF₂₀ recorded in CD₂Cl₂ (500 MHz) at room temperature.



Figure S42. ¹H-NMR spectrum of Bz **F**cBArF₂₀ recorded in acetone- d_6 (500 MHz) at room temperature.



Figure S43. ¹H-NMR spectrum of Bz **Fc**BArF₂₀ recorded in CD₂Cl₂ (500 MHz) at room temperature.



Figure S44. ¹⁹F-NMR spectrum of Melo **Fc**BArF₂₀ recorded in acetone- d_6 (470 MHz) at room temperature.



Figure S45. ¹⁹F-NMR spectrum of ^{*Me2*}**Fc**BArF₂₀ recorded in acetone-*d*₆ (470 MHz) at room temperature.



Figure S46. ¹⁹F-NMR spectrum of ^{Me2}FcBArF₂₀ recorded in CD₂Cl₂ (470 MHz) at room temperature.



Figure S47. ¹⁹F-NMR spectrum of ^{*nBu*}FcBArF₂₀ recorded in acetone-*d*₆ (470 MHz) at room temperature.



Figure S48. ¹⁹F-NMR spectrum of nBu **Fc**BArF₂₀ recorded in CD₂Cl₂ (470 MHz) at room temperature.



Figure S49. ¹⁹F-NMR spectrum of **Fc**BArF₂₀ recorded in acetone-*d*₆ (470 MHz) at room temperature.



Figure S50. ¹⁹F-NMR spectrum of ^{*B*}**Fc**BArF₂₀ recorded in acetone-*d*₆ (470 MHz) at room temperature.



Figure S51. ¹⁹F-NMR spectrum of ^{Br}FcBArF₂₀ recorded in CD₂Cl₂ (470 MHz) at room temperature.



Figure S52. ¹⁹F-NMR spectrum of A_c **Fc**BArF₂₀ recorded in acetone- d_6 (470 MHz) at room temperature.



Figure S53. ¹⁹F-NMR spectrum of ^{Ac}FcBArF₂₀ recorded in CD₂Cl₂ (470 MHz) at room temperature.



Figure S54. ¹⁹F-NMR spectrum of Bz **Fc**BArF₂₀ recorded in acetone- d_6 (470 MHz) at room temperature.



Figure S55. ¹⁹F-NMR spectrum of Bz **Fc**BArF₂₀ recorded in CD₂Cl₂ (470 MHz) at room temperature.



Figure S56. ¹⁹F-NMR spectrum of ^{Br2}FcBArF₂₀ recorded in acetone-*d*₆ (376 MHz) at room temperature.



Figure S57. ¹⁹F-NMR spectrum of Br2 FcBArF₂₀ recorded in CD₂Cl₂ (470 MHz) at room temperature.



Figure S58. ¹⁹F-NMR spectrum of ^{Ac2}**Fc**BArF₂₀ recorded in CD₂Cl₂ (470 MHz) at room temperature.



Figure S59. ¹⁹F-NMR spectra of (a) Bz2 **Fc**[SbF₆], (b) AgSbF₆, and (c) Bz2 **Fc**[SbF₆] in the presence of AgSbF₆ recorded in CD₂Cl₂ (470 MHz) at room temperature.



Figure S60. (a) Perspective view of $[(nBu)_4N][B(C_6F_5)_4]$ showing 50% thermal contours for all non-hydrogen atoms, and (b) diagram illustrating the molecular packing of $[(nBu)_4N][B(C_6F_5)_4]$ at 100 K (hydrogen atoms have been omitted for clarity). Selected bond lengths [Å] and angles [°]: N(1)-C(1), 1.517(2); N(1)-C(5), 1.525(2); N(1)-C(9), 1.521(2); N(1)-C(13), 1.521(2); B(1)-C(17), 1.654(3); B(1)-C(23), 1.651(3); B(1)-C(29), 1.663(3); B(1)-C(35), 1.649(3); C(1)-N(1)-C(9), 105.65(13); C(1)-N(1)-C(13), 111.46(14); C(9)-N(1)-C(13), 111.32(13); C(1)-N(1)-C(5), 111.28(13); C(9)-N(1)-C(5), 110.78(13); C(13)-N(1)-C(5), 106.43(13); C(17)-B(1)-C(29), 113.94(15); C(23)-B(1)-C(17), 112.52(14); C(35)-B(1)-C(29), 113.57(14); C(23)-B(1)-C(29), 100.74(13).



Figure S61. (a) Perspective view of $[Ag(MeCN)_4][B(C_6F_5)_4]$ showing 50% thermal contours for all non-hydrogen atoms, and (b) diagram illustrating the molecular packing of $[Ag(MeCN)_4][B(C_6F_5)_4]$ at 100 K (hydrogen atoms have been omitted for clarity). Selected bond lengths [Å] and angles [°]: Ag(1)-N(1), 2.242(2); Ag(1)-N(2), 2.283(2); Ag(1)-N(3), 2.313(2); Ag(1)-N(4), 2.314(2); B(1)-C(9), 1.648(3); B(1)-C(15), 1.652(3); B(1)-C(21), 1.654(3); B(1)-C(27), 1.656(3); N(1)-Ag(1)-N(2), 102.37(7); N(1)-Ag(1)-N(3), 106.30(7); N(2)-Ag(1)-N(3), 121.47(8); N(1)-Ag(1)-N(4), 136.27(7); N(2)-Ag(1)-N(4), 101.95(8); N(3)-Ag(1)-N(4), 90.89(7); C(9)-B(1)-C(15), 101.98(16); C(9)-B(1)-C(21), 114.80(16); C(15)-B(1)-C(21), 113.40(16); C(9)-B(1)-C(27), 112.50(16); C(15)-B(1)-C(27), 114.20(16); C(21)-B(1)-C(27), 100.54(15).



Figure S62. Diagram illustrating the molecular packing of Me10 **F**cBArF₂₀ at 100 K (hydrogen atoms have been omitted for clarity).



Figure S63. Diagram illustrating the molecular packing of Me2 **Fc**BArF₂₀ at 100 K (hydrogen atoms have been omitted for clarity).



Figure S64. Diagram illustrating the molecular packing of nBu **Fc**BArF₂₀ at 100 K (hydrogen atoms have been omitted for clarity).



Figure S65. Diagram illustrating the molecular packing of ^B**Fc**BArF₂₀ at 100 K (hydrogen atoms have been omitted for clarity).



Figure S66. Diagram illustrating the molecular packing of ${}^{Ac}\mathbf{Fc}BArF_{20}$ at 100 K (hydrogen atoms have been omitted for clarity).



Figure S67. Diagram illustrating the molecular packing of ${}^{Bz}\mathbf{Fc}BArF_{20}$ at 100 K (hydrogen atoms have been omitted for clarity).



Figure S68. Diagram illustrating the molecular packing of Br_2 **Fc**BArF₂₀ at 100 K (hydrogen atoms have been omitted for clarity).



Figure S69. Diagram illustrating the molecular packing of Ac2 **Fc**BArF₂₀ at 100 K (hydrogen atoms have been omitted for clarity).



Figure S70. Diagram illustrating the molecular packing of Bz2 **Fc**[SbF₆] at 100 K (hydrogen atoms have been omitted for clarity).



Figure S71. Plot showing the changes in the Ct…Ct distances (red) and in the Fe– C_{avg} distances (blue) upon one electron oxidation of the ferrocene derivatives discussed in this study.

2. Tables for IR Spectroscopy and X-Ray Crystallography Data

a. Comparison of IR Data

	^{Me10} Fc	Me10 Fc BArF ₂₀	^{Me2} Fc	Me2 Fc BArF ₂₀	^{<i>nBu</i>} Fc	^{<i>nBu</i>} Fc BArF ₂₀	Fc	FcBArF ₂₀
							3105	
ν (C-H): C ₅ H ₅	-	-	3077	3115	3091	3128	3093	3128
							3093	
	2964	2097	2968	2934	2956	2960		
ν(C-H): CH ₃	2944	2987	2944	2919	2926	2934		
	2882	2978	2916	2895	2870	2876	-	-
	2850	2925	2880	2877	2856	2865		

Table S1. IR spectral data (cm^{-1}) for the ferrocene and ferricenium derivatives studied.

Table S2. IR spectral data (cm⁻¹) for the ferrocene and ferricenium derivatives studied.

	^B F c	^{Br} Fc BArF ₂₀	^{Ac} Fc	Ac Fc BArF ₂₀	^{Br2} Fc	^{Br2} Fc BArF ₂₀	Ac2 Fc	Ac2 Fc BArF ₂₀
ν(C-H): C ₅ H ₅	3107 3096	3124 3114	3287	3377	3102 3094	3133 3124	3295	3377
	3085	3102	3308		3085	3101		
ν(C-H): CH ₃	-	-	3116309730773068	3140 3125 3115 3092	-	-	3104 3087 3074	3117 3104
ν(C-H): C ₆ H ₅	-	-	-	-	-	-	-	-
v(C=O)	-	-	1650	1698	-	-	1650	1697

	^{Bz} Fc	Bz Fc BArF ₂₀	^{Bz2} Fc	^{Bz2} Fc [SbF ₆]
	3239	3298	3247	3308
	3114	3103	3109	3123
ν (C-H): C ₆ H ₅ /C ₅ H ₅	3092	3082	3100	3112
	3066	2981	3084	3100
	2967	2965	3070	3068
ν(C=O)	1624	1659	1630	1665
v(SbF ₆)	-	-	-	651

Table S3. IR spectral data (cm^{-1}) for the ferrocene and ferricenium derivatives studied.

Table S4. Average ${}^{3}J$ (${}^{1}H-{}^{1}H$)-values calculated for ferrocene and its derivatives from the two proton signals (triplets) of the substituted Cp rings.

Compound	Avg. Cp $^{3}J(^{1}H-^{1}H)$ value (Hz)	NMR Magnet Strength (MHz)
^{Bz2} Fc	1.84	500
^{Ac2} Fc	1.94	500
^{Br2} Fc	1.85	400
^{Bz} Fc	1.75	500
^{Ac} Fc	1.95	500
^{Br} Fc	1.88	500
Fc		500
^{nBu} Fc	1.83	500
^{Me2} Fc	1.63	500
^{Me10} Fc		500

b. Crystallography Data and Data Collection Parameters

Table S5. Crystallographic Data and Data Collection Parameter	rs.
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	$[(nBu)_4N][B(C_6F_5)_4]$	$[Ag(MeCN)_4][B(C_6F_5)_4]$
Formula	$C_{40}H_{36}BF_{20}$ N	$C_{32}H_{12}AgBF_{20}N_4$
T (K)	100(2)	100(2)
Formula weight	921.51	951.14
Crystal system	Monoclinic	Monoclinic
Space group	Cc	<i>P</i> 2 ₁ /c
<i>a,</i> Å	23.9161(5)	10.9055(6)
<i>b,</i> Å	12.8024(3)	16.9646(4)
c, Å	17.3043(4)	19.0513(15)
a, deg	90	90
β, deg	130.542(2)	104.764(9)
γ, deg	90	90
<i>V</i> , Å3	4026.33(18)	3408.3(4)
Ζ	4	4
Radiation (λ, Å)	Μο Κα (0.71073)	Μο Κα (0.71073)
dcalcd, g•cm ⁻³	1.520	1.854
F(000)	1872	1856
Crystal size (mm ³)	0.565 x 0.523 x 0.320	0.406 x 0.184 x 0.116
Theta range for data collection	2.365 to 27.500°	2.274 to 25.499°
μ , mm ⁻¹	0.153	0.734
No of unique data	9127	6352
Completeness to theta	99.9%	99.9%
No. of restraints	2	0
No. of params. refined	563	527
GOF on F ²	1.036	1.030
$R1^{a[I>2\sigma(I)]}$	0.0247	0.0278
R1ª (all data)	0.0265	0.0368
$wR2^{b}$ (all data)	0.0621	0.0676
Largest diff. peak and hole	0.192 and -0.163 e.Å ⁻³	0.488 and -0.720 e.Å ⁻³

^aR1=
$$\frac{\Sigma ||F_o| - |F_c||}{\Sigma |F_o|}$$
; ^bwR2= $\sqrt{\frac{\Sigma [w(F_o^2 - F_c^2)^2]}{\Sigma [w(F_o^2)^2]}}$

	Me10 Fc BArF ₂₀	Me2 Fc BArF ₂₀	^{<i>nBu</i>} Fc BArF ₂₀
Formula	$C_{44}H_{30}BF_{20}Fe$	$C_{36}H_{14}BF_{20}Fe$	$C_{38}H_{18}BF_{20}Fe$
T (K)	100(2)	100(2)	100(2)
Formula weight	1005.34	893.13	921.18
Crystal system	Monoclinic	Orthorhombic	Triclinic
Space group	<i>P</i> 2 ₁ /c	P bcn	P -1
a, Ă	16.5730(4)	20.9252(4)	15.4902(6)
<i>b,</i> Å	19.8456(5)	29.1241(4)	15.5939(6)
<i>c,</i> Ă	24.3129(5)	31.8841(4)	16.4411(5)
α, deg	90	90	107.224(3)
β, deg	90.297	90	102.664(3)°
γ, deg	90	90	101.494(4)°
<i>V</i> , Å3	7996.4(3)	19431.0(5)	3549.2(2)
Ζ	8	24	4
Radiation (λ , Å)	Μο Κα (0.71073)	Μο Κα (0.71073)	Μο Κα (0.71073)
dcalcd, g∙cm-3	1.670	1.832	1.724
F(000)	4040	10584	1828
Crystal size (mm ³)	0.29 x 0.25 x 0.14	0.351 x 0.272 x 0.107	0.285 x 0.109 x 0.075
Theta range for data collection	2.217 to 24.999°	1.751 to 25.500°	2.226 to 27.500°
μ , mm ⁻¹	0.505	0.611	0.561
No of unique data	14294	17808	16303
Completeness to theta	99.9%	98.7%	99.9%
No. of restraints	24	54	0
No. of params. refined	1213	1694	1109
GOF on <i>F</i> ²	0.973	1.113	1.007
$R1^{a [I> 2\sigma(I)]}$	0.0463	0.0531	0.0458
R1ª (all data)	0.0750	0.0707	0.0917
wR2 ^b (all data)	0.1102	0.1346	0.0979
Largest diff. peak and hole	0.526 and -0.383 e.Å ⁻³	2.017 and -0.777 e.Å $^{-3}$	0.669 and -0.485 e.Å ⁻³

 Table S6. Crystallographic Data and Data Collection Parameters.

^aR1=
$$\frac{\Sigma ||F_o| - |F_c||}{\Sigma |F_o|}$$
; ^bwR2= $\sqrt{\frac{\Sigma [w(F_o^2 - F_c^2)^2]}{\Sigma [w(F_o^2)^2]}}$

	^{Br} Fc BArF ₂₀	Ac Fc BArF ₂₀	^B zFc BArF ₂₀
Formula	C ₃₄ H ₉ BBrF ₂₀ Fe	$C_{36}H_{12}BF_{20}FeO$	$C_{41}H_{14}BF_{20}FeO$
Т (К)	100(2)	100(2)	100(2)
Formula weight	943.98	907.12	969.18
Crystal system	Monoclinic	Triclinic	Triclinic
Space group	<i>P</i> 2 ₁ /n	P -1	P -1
<i>a,</i> Å	14.3172(3)	8.5444(3)	11.5342(4)
<i>b</i> , Å	13.0057(3)	12.5527(5)	12.1297(6)
<i>c,</i> Å	16.3446(3)	16.3063(6)	15.3574(7)
α, deg	90	73.244(3)°	108.024(4)
β , deg	90.457(2)	88.652(3)°	94.966(3)
γ, deg	90	73.301(4)°	115.789(4)
V, Å3	3043.35(11)	1600.70(11)	1777.22(15)
Ζ	4	2	2
Radiation (λ , Å)	Μο Κα (0.71073)	Μο Κα (0.71073)	Μο Κα (0.71073)
dcalcd, g∙cm-3	2.060	1.882	1.811
F(000)	1836	894	958
Crystal size (mm ³)	0.293 x 0.107 x 0.097	0.158 x 0.137 x 0.120	0.276 x 0.218 x 0.116
Theta range for data collection	2.450 to 27.496°	2.492 to 25.497°	2.355 to 25.498°
μ , mm ⁻¹	1.961	0.622	0.567
No of unique data	6969	5955	6611
Completeness to theta	99.9%	99.9%	99.9%
No. of restraints	0	0	0
No. of params. refined	514	533	577
GOF on F^2	1.024	1.052	1.030
$R1^{a[I>2\sigma(I)]}$	0.0256	0.0341	0.0288
R1ª (all data)	0.0346	0.0521	0.0382
wR2 ^b (all data)	0.0586	0.0718	0.0656
Largest diff. peak and hole	0.413 and -0.349 e.Å ⁻³	0.328 and -0.309 e.Å $^{-3}$	$0.336 \text{ and } -0.369 \text{ e.}\text{\AA}^{-3}$

Table S7. Crystallographic Data and Data Collection Parameters.

^aR1=
$$\frac{\Sigma||F_o|-|F_c||}{\Sigma|F_o|}$$
; ^bwR2= $\sqrt{\frac{\Sigma[w(F_o^2-F_c^2)^2]}{\Sigma[w(F_o^2)^2]}}$

	^{Br2} Fc BArF ₂₀	Ac2 Fc BArF ₂₀	Bz2 Fc [SbF ₆]	
Formula	$C_{34}H_8BBr_2F_{20}Fe$	$C_{38}H_{14}BF_{20}FeO_2$	$C_{24}H_{18}F_6FeO_2Sb$	
T (K)	100(2)	100(2)	100(2)	
Formula weight	1022.88	949.15	629.98	
Crystal system	Monoclinic	Monoclinic	Triclinic	
Space group	$P 2_1/n$	<i>P</i> 2 ₁ /c	P -1	
<i>a,</i> Å	15.4399(13)	15.4200(8)	7.7836(4)	
<i>b,</i> Å	13.3339(7)	16.6840(5)	8.1200(5)	
<i>c,</i> Å	15.7029(10)	15.1965(8)	9.8619(7)	
α, deg	90	90	112.789(6)	
β , deg	91.482(6)	119.448(7)	101.780(5)	
γ, deg	90	90	96.453(5)	
<i>V</i> , Å3	3231.7(4)	3404.5(3)	549.74(6)	
Ζ	4	4	1	
Radiation (λ , Å)	Mo Ka (0.71073)	Mo Ka (0.71073)	Μο Κα (0.71073)	
dcalcd, g∙cm-3	2.102	1.852	1.903	
F(000)	1972	1876	309	
Crystal size (mm ³)	0.141 x 0.095 x 0.073	0.270 x 0.125 x 0.111	0.290 x 0.195 x 0.190	
Theta range for data collection	2.418 to 25.497°	2.442 to 27.500°	2.735 to 27.497°	
μ , mm ⁻¹	3.085	0.592	1.949	
No of unique data	6002	7816	2511	
Completeness to theta	99.8%	99.9%	99.5%	
No. of restraints	0	0	0	
No. of params. refined	523	561	157	
GOF on F^2	1.011	1.015	1.056	
$R1^{a \lfloor I > 2\sigma(I) \rfloor}$	0.0438	0.0355	0.0176	
R1ª (all data)	0.0958	0.0542	0.0180	
$wR2^{b}$ (all data)	0.0803	0.0786	0.0453	
Largest diff. peak and hole	0.473 and -0.581 e.Å ⁻³	0.390 and -0.424 e.Å ⁻³	0.388 d -0.434 e.Å ⁻³	

 Table S8. Crystallographic Data and Data Collection Parameters.

$${}^{a}R1 = \frac{\Sigma ||F_{o}| - |F_{c}||}{\Sigma |F_{o}|}; {}^{b}wR2 = \sqrt{\frac{\Sigma [w(F_{o}^{2} - F_{c}^{2})^{2}]}{\Sigma [w(F_{o}^{2})^{2}]}}$$

c. Selected Structural Parameters for All the Ferrocene and Ferricenium Derivatives Described in This Study

Table S9. Selected structural parameters of the neutral and oxidized complexes.

	$C-C^a$	$C-C^a$	Fe-C _{avg} ^b	Fe-C _{avg} ^b	CtFe ^c	CtFe ^c	$Ct \cdots Ct^d$	_
Complex	(Å) (T)	(Å) (B)	(Å) (T)	(Å) (B)	(Å) (T)	(Å) (B)	(Å)	Reference
Me10 Fc	1.434	1.434	2.053	2.053	1.651	1.651	3.305	1
$^{Me10}\mathbf{Fc}^+$	1.432	1.430	2.095	2.098	1.706	1.711	3.413	this work
^{Me2} Fc	1.430	1.428	2.047	2.047	1.646	1.647	3.293	1
$^{Me2}\mathbf{Fc}^+$	1.416	1.412	2.104	2.109	1.730	1.733	3.463	this work
^R Fc ^{+e}	1.424	1.414	2.045	2.041	1.648	1.650	3.297	2
$^{nBu}\mathbf{Fc}^{+}$	1.412	1.410	2.083	2.083	1.702	1.703	3.404	this work
Fc	1.427	1.425	2.046	2.046	1.648	1.649	3.296	3
Fc ⁺	1.394	1.391	2.079	2.075	1.708	1.705	3.412	4
^{Br} Fc	1.424	1.420	2.041	2.048	1.642	1.654	3.296	5
${}^{Br}\mathbf{Fc}^+$	1.417	1.410	2.089	2.082	1.706	1.701	3.407	this work
^{Ac} Fc	1.429	1.426	2.045	2.048	1.645	1.651	3.294	6
$^{Ac}\mathbf{Fc}^{+}$	1.417	1.408	2.092	2.084	1.711	1.705	3.415	this work
^{Bz} Fc	1.423	1.408	2.043	2.043	1.646	1.655	3.301	7
$B^{Bz}\mathbf{Fc}^{+}$	1.418	1.401	2.094	2.085	1.712	1.711	3.423	this work
^{Br2} Fc	1.429	1.427	2.048	2.049	1.648	1.650	3.298	8
$^{Br2}\mathbf{Fc}^{+}$	1.415	1.411	2.088	2.080	1.706	1.700	3.405	this work
^{Ac2} Fc	1.431	1.432	2.049	2.050	1.649	1.649	3.293	1
$^{Ac2}\mathbf{Fc}^{+}$	1.420	1.417	2.092	2.091	1.708	1.709	3.417	this work
^{Bz2} Fc	1.417	1.417	2.040	2.044	1.646	1.650	3.296	9
$^{Bz2}\mathbf{Fc}^{+}$	1.420	1.420	2.089	2.089	1.705	1.705	3.409	this work

T and *B* correspond to the top and bottom Cp rings in all complexes, respectively. The Top ring is the substituted ring in the monosubstituted complexes. ^{*a*}Average of the C–C bond lengths for each Cp ring. ^{*b*}Average of the Fe–C(Cp) bond lengths with each Cp ligand. ^{*c*}Distance between the centroid of the Cp ring and Fe center. ^{*d*}Separation between the centroids of two Cp rings. ^{*e*}The data corresponds to average for the two closely related ferrocene derivatives, nCl4 Fc and Fc-(CH₂)₈-Fc.
Table S10. Selected structural and geometrical parameters of the neutral and oxidized complexes.

Complex	Ct-Fe-Ct, ∠α (°)	Ring tilt, $\angle \beta(T)$ (°)	Ring tilt, $\angle \beta(B)(^\circ)$	Torsion, ∠φ (°)	Sub. out of plane $\angle \gamma (T) (^{\circ})^{a}$	Sub. out of plane $\angle \gamma$ (B) (°) ^{<i>a</i>}	Reference
Me10 Fc	180.0	90.0	90.0	36.0	-1.78	-1.78	1
Me10 Fc ⁺	179.7	89.6	90.5	16.9/35.9	-1.62	-1.17	this work
Me2 Fc	178.4	90.2	90.4	-3.6	-2.63	-2.27	1
$^{Me2}\mathbf{Fc}^{+}$	179.1	96.4	85.5	13.6/-14.9/-1.9	+0.45	-0.90	this work
$^{R}\mathbf{Fc}^{+b}$	179.5	90.3	89.6	-3.8	-2.6		2
$^{nBu}\mathbf{Fc}^{+}$	178.9	91.2	90.7	7.94/-1.18	+1.19	_	this work
Fc	179.7	90.0	90.0	-8.8/9.0		_	3
\mathbf{Fc}^+	179.1	90.0	90.0	-8.4			4
^{Br} Fc	179.3	89.0	89.7	2.6/28.57	-2.06		5
$B^{Br}\mathbf{Fc}^{+}$	178.8	90.8	90.0	9.1	-2.31		this work
^{Ac} Fc	178.2	89.1	90.2	0.1/1.0	+3.52		6
$^{Ac}\mathbf{Fc}^{+}$	178.2	88.7	88.9	-3.4	+0.78		this work
^{Bz} Fc	177.6	89.4	90.3	6.3	-0.10	_	7
${}^{Bz}\mathbf{Fc}^+$	178.5	90.2	90.7	-1.3	+1.85	_	this work
^{Br2} Fc	177.7	90.0	89.8	0.6	-2.67	-4.07	8
$Br^{2}\mathbf{Fc}^{+}$	177.0	92.5	93.1	3.5	+1.27	+1.06	this work
Ac2 Fc	178.9	89.1	88.9	139.6	+4.37	-2.97	1
$^{Ac2}\mathbf{Fc}^{+}$	179.2	88.3	88.0	-26.4	+2.86	+2.18	this work
^{Bz2} Fc	179.4	89.1	89.3	130.4	+5.06	-3.46	9
$^{Bz2}\mathbf{Fc}^{+}$	180.0	88.4	88.4	180.0	+2.33	+2.33	this work

"For substituent out of plane deviation, "+" denotes towards the Fe center, while "-" denotes away from the Fe center. ^bThe data corresponds to average for the two closely related ferrocene derivatives, nC14 Fc and Fc-(CH₂)₈-Fc.

	Me10 Fc BArF ₂₀	Me2 Fc BArF ₂₀	nBu Fc BArF ₂₀
Fe(1)-C(1A)	2.101(5)	2.028(3)	2.115(3)
Fe(1)-C(2A)	2.099(5)	2.000(3)	2.068(3)
Fe(1)-C(3A)	2.097(5)	2.214(4)	2.055(3)
Fe(1)-C(4A)	2.107(5)	2.176(4)	2.071(3)
Fe(1)-C(5A)	2.110(5)	2.078(4)	2.098(3)
Fe(1)-C(6A)	2.107(5)	2.295(4)	2.097(3)
Fe(1)-C(7A)	2.100(5)	2.170(4)	2.073(3)
Fe(1)-C(8A)	2.083(5)	2.047(4)	2.070(3)
Fe(1)-C(9A)	2.101(5)	1.937(4)	2.084(3)
Fe(1)-C(10A)	2.099(5)	2.053(4)	2.096(3)
Fe(2)-C(1B)	2.115(5)	2.264(5)	2.113(3)
Fe(2)-C(2B)	2.087(5)	2.015(4)	2.104(3)
Fe(2)-C(3B)	2.079(5)	1.965(4)	2.068(3)
Fe(2)-C(4B)	2.081(5)	2.069(4)	2.058(3)
Fe(2)-C(5B)	2.096(5)	2.200(4)	2.081(3)
Fe(2)-C(6B)	-	2.063(4)	2.099(3)
Fe(2)-C(7B)	-	2.116(4)	2.091(3)
Fe(2)-C(8B)	-	2.216(4)	2.078(3)
Fe(2)-C(9B)	-	2.178(4)	2.066(3)
Fe(2)-C(10B)	-	1.980(4)	2.079(3)
Fe(3)-C(1C)	-	2.173(8)	-
Fe(3)-C(2C)	-	2.225(8)	-
Fe(3)-C(3C)	-	2.196(8)	-
Fe(3)-C(4C)	-	1.951(7)	-
Fe(3)-C(5C)	-	2.036(6)	-
Fe(3)-C(6C)	-	2.030(9)	-
Fe(3)-C(7C)	-	2.099(9)	-
Fe(3)-C(8C)	-	2.172(8)	-
Fe(3)-C(9C)	-	2.220(9)	-
Fe(3)-C(10C)	-	2.039(7)	-

	^{Br} Fc BArF ₂₀	$^{Ac}\mathbf{Fc}BArF_{20}$	^{Bz} Fc BArF ₂₀	Br2 Fc BArF ₂₀	Ac2 Fc BArF ₂₀	Bz2 Fc [SbF ₆]
Fe(1)-C(1A)	2.0962(18)	2.073(2)	2.0979(17)	2.116(4)	2.0634(19)	2.0643(16)
Fe(1)-C(2A)	2.0886(18)	2.091(2)	2.0697(18)	2.084(5)	2.0648(18)	2.0938(14)
Fe(1)-C(3A)	2.0843(18)	2.112(2)	2.0718(19)	2.055(5)	2.1010(19)	2.1162(14)
Fe(1)-C(4A)	2.0835(18)	2.107(2)	2.1053(19)	2.068(4)	2.1223(19)	2.1059(14)
Fe(1)-C(5A)	2.0924(18)	2.081(2)	2.1246(18)	2.115(4)	2.105(2)	2.0659(15)
Fe(1)-C(6A)	2.081(2)	2.067(2)	2.096(2)	2.126(4)	2.0593(18)	-
Fe(1)-C(7A)	2.086(2)	2.078(2)	2.070(2)	2.085(4)	2.1003(18)	-
Fe(1)-C(8A)	2.0863(19)	2.096(2)	2.065(2)	2.036(5)	2.136(2)	-
Fe(1)-C(9A)	2.0794(19)	2.097(2)	2.0867(19)	2.050(5)	2.0985(19)	-
Fe(1)-C(10A)	2.075(2)	2.082(2)	2.110(2)	2.105(5)	2.0664(18)	-
Br(1)-C(1)	1.8666(18)	-	-	1.872(5)	-	-
Br(2)-C(6)	-	-	-	1.855(5)	-	-
C(11)-C(1)	-	1.500(3)	1.508(3)	-	1.503(3)	1.500(2)
C(13)-C(6)	-	-	-	-	1.494(3)	-
O(1)-C(11)	-	1.209(3)	1.215(2)	-	1.209(3)	1.2149(19)
O(2)-C(13)	-	-	-	-	1.210(2)	-

Table S12. Selected bond lengths (Å) for the ferricenium complexes containing mildly electron withdrawing substituents.

3. Electrochemistry

a. Uncompensated Resistance and Impedance Measurements.

The uncompensated resistance (R_u) was measured using potentio electrochemical impedance spectroscopy (PEIS) to correct for internal resistance drop of voltage in the electrolyte solution. A three-electrode setup was employed using the same electrolyte/solvent combinations as were used in the ferrocene cyclic voltammetry (CV) experiments. The frequency was scanned from 1 MHz to 100 mHz and the "real impedance" value observed at 1MHz was considered the uncompensated resistance value for that solution. This was corrected 85% in the cyclic voltammetry experiments.

Table S13. Ru Values for Each Solvent/Electrolyte Combination Used in Ferrocene Cyclic Voltammetry Experiments.

Solvent/Electrolyte Solution	R _u Value (Ohm)
$MeCN, [(nBu)_4N][B(C_6F_5)_4]$	67
MeCN, $[(nBu)_4N][PF_6]$	62
DCM, $[(nBu)_4N][B(C_6F_5)_4]$	237
DCM, $[(nBu)_4N][PF_6]$	410
MeTHF, $[(nBu)_4N][B(C_6F_5)_4]$	351

The Ag/AgCl reference electrodes were stored in 0.05 M H_2SO_4 overnight and then in saturated KCl solution immediately prior to testing. Before performing experiments on the ferrocene samples in organic solutions, the impedance of the Ag/AgCl reference electrodes was measured in a 100 mM aqueous KCl solution using impedance spectroscopy in a 2-electrode setup between the counter and reference electrodes. The frequency was scanned from 200 kHz to 1 Hz and the real impedance value observed at 200 kHz was considered the impedance for that particular Ag/AgCl electrode. An impedance under 20,000 Ohm was considered suitable for use. Additionally, CV measurements of ferrocene carboxylate in 100 mM aqueous KCl solution were performed and the measured potential vs Ag/AgCl was compared to the potential observed using a saturated calomel electrode (SCE). A potential difference of approximately 32-44 mV was considered satisfactory for use.¹⁰ If the Ag/AgCl electrode satisfied both of these conditions, it was used in the experiments.

b. Cyclic Voltammograms of All Ferrocenes Discussed in Each Solvent

Each sample solution contained 2 mM of the corresponding ferrocene and 100 mM of the supporting electrolyte. The potentials were collected vs a leak-free Ag/AgCl reference electrode. The working electrode was glassy carbon and the counter electrode was a carbon rod. Scan rates were varied as follows (in mV/s): 1000, 500, 250, 100, 50, 25. Exceptions to this procedure were Me10 Fc; Bc2 Fc; and Ac2 Fc in MeCN, as discussed in the main text.

i. DCM



Figure S72. Cyclic voltammograms at 100 mV/s of various ferrocene derivatives collected in DCM using $[(nBu)_4N][B(C_6F_5)_4]$ as the supporting electrolyte.

ii. MeCN



Figure S73. Cyclic voltammograms at 100 mV/s of various ferrocene derivatives collected in MeCN using $[(nBu)_4N][B(C_6F_5)_4]$ as the supporting electrolyte.



Figure S74. Cyclic voltammograms at 100 mV/s of various ferrocene derivatives collected in MeCN using $[(nBu)_4N][PF_6]$ as the supporting electrolyte.



Figure S75. Cyclic voltammograms at 100 mV/s of various ferrocene derivatives collected in MeTHF using $[(nBu)_4N][B(C_6F_5)_4]$ as the supporting electrolyte.

c. Cyclic Voltammograms of Each Ferrocene Derivative with Their Corresponding Randles-Sevcik Plots

i. Decamethylferrocene



Figure S76. (Left) Cyclic voltammograms of 2 mM Mel0 Fc in DCM with 100 mM $[(nBu)_4N][B(C_6F_5)_4]$ as the supporting electrolyte at different scan rates. (Right) Randles-Sevcik plot of the CV data.



Figure S77. (Left) Cyclic voltammograms of 2 mM Mel0 Fc in DCM with 100 mM $[(nBu)_4N][PF_6]$ as the supporting electrolyte at different scan rates. (Right) Randles-Sevcik plot of the CV data.



Figure S78. (Left) Cyclic voltammograms of 1 mM Mel0 Fc in MeCN with 100 mM $[(nBu)_4N][B(C_6F_5)_4]$ as the supporting electrolyte at different scan rates. (Right) Randles-Sevcik plot of the CV data.



Figure S79. (Left) Cyclic voltammograms of 1 mM^{Mel0} Fc in MeCN with $100 \text{ mM} [(nBu)_4\text{N}][PF_6]$ as the supporting electrolyte at different scan rates. (Right) Randles-Sevcik plot of the CV data.



Figure S80. (Left) Cyclic voltammograms of 2 mM Mel0 Fc in MeTHF with 100 mM $[(nBu)_4N][B(C_6F_5)_4]$ as the supporting electrolyte at different scan rates. (Right) Randles-Sevcik plot of the CV data.



Figure S81. (Left) Cyclic voltammograms of 2 mM^{Me2} **Fc** in DCM with $100 \text{ mM} [(nBu)_4\text{N}][B(C_6F_5)_4]$ as the supporting electrolyte at different scan rates. (Right) Randles-Sevcik plot of the CV data.



Figure S82. (Left) Cyclic voltammograms of 2 mM^{Me2} **Fc** in DCM with $100 \text{ mM}[(n\text{Bu})_4\text{N}][PF_6]$ as the supporting electrolyte at different scan rates. (Right) Randles-Sevcik plot of the CV data.



Figure S83. (A) Cyclic voltammograms of 2 mM Me2 Fc in MeCN with 100 mM $[(nBu)_4N][B(C_6F_5)_4]$ as the supporting electrolyte at different scan rates. (B) Randles-Sevcik plot of the CV data.



Figure S84. (Left) Cyclic voltammograms of 2 mM Me2 **Fc** in MeCN with 100 mM $[(nBu)_4N][PF_6]$ as the supporting electrolyte at different scan rates. (Right) Randles-Sevcik plot of the CV data.



Figure S85. (Left) Cyclic voltammograms of 2 mM Me2 Fc in MeTHF with 100 mM $[(nBu)_4N][B(C_6F_5)_4]$ as the supporting electrolyte at different scan rates. (Right) Randles-Sevcik plot of the CV data.

iii. n-Butylferrocene



Figure S86. (Left) Cyclic voltammograms of 2 mM nBu Fc in DCM with 100 mM $[(nBu)_4N][B(C_6F_5)_4]$ as the supporting electrolyte at different scan rates. (Right) Randles-Sevcik plot of the CV data.



Figure S87. (Left) Cyclic voltammograms of 2 mM nBu Fc in DCM with 100 mM [$(nBu)_4$ N][PF₆] as the supporting electrolyte at different scan rates. (Right) Randles-Sevcik plot of the CV data.



Figure S88. (Left) Cyclic voltammograms of 2 mM ^{*nBu*}**Fc** in MeCN with 100 mM $[(nBu)_4N][B(C_6F_5)_4]$ as the supporting electrolyte at different scan rates. (Right) Randles-Sevcik plot of the CV data.



Figure S89. (Left) Cyclic voltammograms of 2 mM nBu Fc in MeCN with 100 mM $[(nBu)_4N]$ [PF₆] as the supporting electrolyte at different scan rates. (Right) Randles-Sevcik plot of the CV data.



Figure S90. (Left) Cyclic voltammograms of 2 mM nBu Fc in MeTHF with 100 mM $[(nBu)_4N][B(C_6F_5)_4]$ as the supporting electrolyte at different scan rates. (Right) Randles-Sevcik plot of the CV data.

iv. Ferrocene



Figure S91. (Left) Cyclic voltammograms of 2 mM Fc in DCM with 100 mM $[(nBu)_4N][B(C_6F_5)_4]$ as the supporting electrolyte at different scan rates. (Right) Randles-Sevcik plot of the CV data.



Figure S92. (Left) Cyclic voltammograms of 2 mM **Fc** in DCM with 100 mM $[(nBu)_4N][PF_6]$ as the supporting electrolyte at different scan rates. (Right) Randles-Sevcik plot of the CV data.



Figure S93. (Left) Cyclic voltammograms of 2 mM **Fc** in MeCN with 100 mM $[(nBu)_4N][B(C_6F_5)_4]$ as the supporting electrolyte at different scan rates. (Right) Randles-Sevcik plot of the CV data.



Figure S94. (Left) Cyclic voltammograms of 2 mM **Fc** in MeCN with 100 mM $[(nBu)_4N][PF_6]$ as the supporting electrolyte at different scan rates. (Right) Randles-Sevcik plot of the CV data.



Figure S95. (Left) Cyclic voltammograms of 2 mM **Fc** in MeTHF with 100 mM $[(nBu)_4N][B(C_6F_5)_4]$ as the supporting electrolyte at different scan rates. (Right) Randles-Sevcik plot of the CV data.

v. 1-Bromoferrocene



Figure S96. (Left) Cyclic voltammograms of 2 mM ^{*B*}**Fc** in DCM with 100 mM $[(nBu)_4N][B(C_6F_5)_4]$ as the supporting electrolyte at different scan rates. (Right) Randles-Sevcik plot of the CV data.



Figure S97. (Left) Cyclic voltammograms of 2 mM ^B**Fc** in DCM with 100 mM $[(nBu)_4N][PF_6]$ as the supporting electrolyte at different scan rates. (Right) Randles-Sevcik plot of the CV data.



Figure S98. (Left) Cyclic voltammograms of 2 mM ^{*Br*}**Fc** in MeCN with 100 mM $[(nBu)_4N][B(C_6F_5)_4]$ as the supporting electrolyte at different scan rates. (Right) Randles-Sevcik plot of the CV data.



Figure S99. (Left) Cyclic voltammograms of $2 \text{ mM}^{Br}\mathbf{Fc}$ in MeCN with $100 \text{ mM}[(nBu)_4\text{N}][PF_6]$ as the supporting electrolyte at different scan rates. (Right) Randles-Sevcik plot of the CV data.



Figure S100. (Left) Cyclic voltammograms of 2 mM ^{*Br*}**Fc** in MeTHF with 100 mM $[(nBu)_4N][B(C_6F_5)_4]$ as the supporting electrolyte at different scan rates. (Right) Randles-Sevcik plot of the CV data.

vi. 1-Acetylferrocene



Figure S101. (Left) Cyclic voltammograms of 2 mM ^{*Ac*}**Fc** in DCM with 100 mM $[(nBu)_4N][B(C_6F_5)_4]$ as the supporting electrolyte at different scan rates. (Right) Randles-Sevcik plot of the CV data.



Figure S102. (Left) Cyclic voltammograms of 2 mM Ac Fc in DCM with 100 mM [$(nBu)_4N$][PF₆] as the supporting electrolyte at different scan rates. (Right) Randles-Sevcik plot of the CV data.



Figure S103. (Left) Cyclic voltammograms of 2 mM ^{*Ac*}**Fc** in MeCN with 100 mM $[(nBu)_4N][B(C_6F_5)_4]$ as the supporting electrolyte at different scan rates. (Right) Randles-Sevcik plot of the CV data.



Figure S104. (Left) Cyclic voltammograms of 2 mM ^{*Ac*}**Fc** in MeCN with 100 mM $[(nBu)_4N][PF_6]$ as the supporting electrolyte at different scan rates. (Right) Randles-Sevcik plot of the CV data.



Figure S105. (Left) Cyclic voltammograms of 2 mM ^{*Ac*}**Fc** in MeTHF with 100 mM $[(nBu)_4N][B(C_6F_5)_4]$ as the supporting electrolyte at different scan rates. (Right) Randles-Sevcik plot of the CV data.



vii. 1-Benzoylferrocene

Figure S106. (Left) Cyclic voltammograms of 2 mM Bz Fc in DCM with 100 mM $[(nBu)_4N][B(C_6F_5)_4]$ as the supporting electrolyte at different scan rates. (Right) Randles-Sevcik plot of the CV data.



Figure S107. (Left) Cyclic voltammograms of 2 mM Bz Fc in DCM with 100 mM [$(nBu)_4N$][PF₆] as the supporting electrolyte at different scan rates. (Right) Randles-Sevcik plot of the CV data.



Figure S108. (Left) Cyclic voltammograms of 2 mM Bz Fc in MeCN with 100 mM $[(nBu)_4N][B(C_6F_5)_4]$ as the supporting electrolyte at different scan rates. (Right) Randles-Sevcik plot of the CV data.



Figure S109. (Left) Cyclic voltammograms of 2 mM Bz **Fc** in MeCN with 100 mM [$(nBu)_4$ N][PF₆] as the supporting electrolyte at different scan rates. (Right) Randles-Sevcik plot of the CV data.



Figure S110. (Left) Cyclic voltammograms of 2 mM Bz Fc in MeTHF with 100 mM $[(nBu)_4N][B(C_6F_5)_4]$ as the supporting electrolyte at different scan rates. (Right) Randles-Sevcik plot of the CV data.



Figure S111. (Left) Cyclic voltammograms of 2 mM Br_2 Fc in DCM with 100 mM $[(nBu)_4N][B(C_6F_5)_4]$ as the supporting electrolyte at different scan rates. (Right) Randles-Sevcik plot of the CV data.



Figure S112. (Left) Cyclic voltammograms of 2 mM Br_2 Fc in DCM with 100 mM $[(nBu)_4N][PF_6]$ as the supporting electrolyte at different scan rates. (Right) Randles-Sevcik plot of the CV data.



Figure S113. (Left) Cyclic voltammograms of 2 mM Br_2 Fc in MeCN with 100 mM $[(nBu)_4N][B(C_6F_5)_4]$ as the supporting electrolyte at different scan rates. (Right) Randles-Sevcik plot of the CV data.



Figure S114. (Left) Cyclic voltammograms of 2 mM Br2 Fc in MeCN with 100 mM [$(nBu)_4$ N][PF₆] as the supporting electrolyte at different scan rates. (Right) Randles-Sevcik plot of the CV data.



Figure S115. (Left) Cyclic voltammograms of 2 mM Br_2 Fc in MeTHF with 100 mM $[(nBu)_4N][B(C_6F_5)_4]$ as the supporting electrolyte at different scan rates. (Right) Randles-Sevcik plot of the CV data.



ix. 1,1'-Diacetylferrocene

Figure S116. (Left) Cyclic voltammograms of 2 mM Ac2 Fc in DCM with 100 mM $[(nBu)_4N][B(C_6F_5)_4]$ as the supporting electrolyte at different scan rates. (Right) Randles-Sevcik plot of the CV data.



Figure S117. (Left) Cyclic voltammograms of 2 mM Ac2 Fc in DCM with 100 mM $[(nBu)_4N][PF_6]$ as the supporting electrolyte at different scan rates. (Right) Randles-Sevcik plot of the CV data.



Figure S118. (Left) Cyclic voltammograms of 2 mM Ac2 Fc in MeCN with 100 mM $[(nBu)_4N][B(C_6F_5)_4]$ as the supporting electrolyte at different scan rates. (Right) Randles-Sevcik plot of the CV data.



Figure S119. (Left) Cyclic voltammograms of 2 mM Ac2 Fc in MeCN with 100 mM $[(nBu)_4N][PF_6]$ as the supporting electrolyte at different scan rates. (Right) Randles-Sevcik plot of the CV data.



Figure S120. (Left) Cyclic voltammograms of 2 mM Ac2 Fc in MeTHF with 100 mM $[(nBu)_4N][B(C_6F_5)_4]$ as the supporting electrolyte at different scan rates. (Right) Randles-Sevcik plot of the CV data.

x. 1,1'-Dibenzoylferrocene



Figure S121. (Left) Cyclic voltammograms of 2 mM Bz2 Fc in DCM with 100 mM $[(nBu)_4N][B(C_6F_5)_4]$ as the supporting electrolyte at different scan rates. (Right) Randles-Sevcik plot of the CV data.



Figure S122. (Left) Cyclic voltammograms of 2 mM Bz2 Fc in DCM with 100 mM $[(nBu)_4N][PF_6]$ as the supporting electrolyte at different scan rates. (Right) Randles-Sevcik plot of the CV data.



Figure S123. (Left) Cyclic voltammograms of 2 mM Bz2 Fc in MeCN with 100 mM $[(nBu)_4N][B(C_6F_5)_4]$ as the supporting electrolyte at different scan rates. (Right) Randles-Sevcik plot of the CV data. We were unable to determine a cathodic peak at 100 mV/s.



Figure S124. (Left) Cyclic voltammograms of 2 mM Bz2 Fc in MeCN with 100 mM [(*n*Bu)₄N][PF₆] as the supporting electrolyte at different scan rates. (Right) Randles-Sevcik plot of the CV data. We were unable to determine a cathodic peak at 100 mV/s.



Figure S125. (Left) Cyclic voltammograms of 2 mM Bz2 Fc in MeTHF with 100 mM $[(nBu)_4N][B(C_6F_5)_4]$ as the supporting electrolyte at different scan rates. (Right) Randles-Sevcik plot of the CV data.

d. Reversibility Data

i. Plots of $\Delta E_{\ensuremath{\mathcal{V}}\xspace_2}$ vs Scan Rate for Each Ferrocene Derivative in Various Media

Overall, in most cases the smallest and largest $\Delta E_{\frac{1}{2}}$ values were found in MeCN and DCM, respectively, both with $[(nBu)_4N][PF_6]$ as the supporting electrolyte. Also, the scan rate has the least influence on the $\Delta E_{\frac{1}{2}}$ values of different ferrocene derivatives in acetonitrile, see below. In general, in low polarity solvents the increased currents, due to the faster scan rates, lead to greater peak-to-peak separations due to larger incomplete *iR* compensation.



Figure S126. Plots of $\Delta E_{\frac{1}{2}}$ vs scan rate for cyclic voltammograms of Mel0 Fc measured in various solvent/electrolyte conditions.



Figure S127. Plots of $\Delta E_{\frac{1}{2}}$ vs scan rate for cyclic voltammograms of Me2 **Fc** measured in various solvent/electrolyte conditions.



Figure S128. Plots of $\Delta E_{\frac{1}{2}}$ vs scan rate for cyclic voltammograms of nBu **Fc** measured in various solvent/electrolyte conditions.



Figure S129. Plots of $\Delta E_{\frac{1}{2}}$ vs scan rate for cyclic voltammograms of **Fc** measured in various solvent/electrolyte conditions.



Figure S130. Plots of $\Delta E_{1/2}$ vs scan rate for cyclic voltammograms of ^B**Fc** measured in various solvent/electrolyte conditions.



Figure S131. Plots of $\Delta E_{\frac{1}{2}}$ vs scan rate for cyclic voltammograms of ^{*Ac*}**Fc** measured in various solvent/electrolyte conditions.



Figure S132. Plots of $\Delta E_{\frac{1}{2}}$ vs scan rate for cyclic voltammograms of Bz Fc measured in various solvent/electrolyte conditions.



Figure S133. Plots of $\Delta E_{\frac{1}{2}}$ vs scan rate for cyclic voltammograms of ^{Br2}**Fc** measured in various solvent/electrolyte conditions.



Figure S134. Plots of $\Delta E_{\frac{1}{2}}$ vs scan rate for cyclic voltammograms of Ac2 Fc measured in various solvent/electrolyte conditions.



Figure S135. Plots of $\Delta E_{\frac{1}{2}}$ vs scan rate for cyclic voltammograms of Bz2 **Fc** measured in various solvent/electrolyte conditions.

ii. Peak Current Ratios (i_{pa}/i_{pc})

Table S14. i_{pa}/i_{pc} values of various ferrocene analogs at 100 mV/s. We were unable to measure a cathodic peak height for ^{Bz2}Fc in MeCN at 100 mV/s; therefore, a ratio of peak heights was not possible. The value in the parentheses corresponds to the most ideal ratio found when the scan rate was increased to 500, ^a 1500, ^b or 1250 mV/s.^c

i _{pa} /i _{pc} in DCM			i_{pa}/i_{pc} in Me	i_{pa}/i_{pc} in MeTHF	
Ferrocene Derivatives	$[(n\mathrm{Bu})_4\mathrm{N}][\mathrm{B}(\mathrm{C}_6\mathrm{F}_5)_4]$	[(<i>n</i> Bu) ₄ N][PF ₆]	$[(nBu)_4N][B(C_6F_5)_4]$	[(<i>n</i> Bu) ₄ N][PF ₆]	$[(nBu)_4N][B(C_6F_5)_4]$
^{Me10} Fc	0.99	0.96	0.98	0.97	1.04
^{Me2} Fc	1.10	0.97	0.99	0.99	0.97
^{<i>nBu</i>} Fc	1.01	0.99	1.00	1.00	1.00
Fc	0.98	0.98	0.97	0.98	0.99
^{Br} Fc	1.07	0.98	0.99	1.01	1.02
^{Ac} Fc	1.07	0.98	1.00	1.04	1.01
^{Bz} Fc	1.02	0.99	1.00	1.02	1.02
^{Br2} Fc	1.01	1.00	1.05	1.04	1.07
^{Ac2} Fc	1.08	1.00	$1.14(1.04)^{a}$	1.29 (1.13) ^b	1.07
^{Bz2} Fc	1.00	1.03	N/A (1.19)°	N/A (1.24) ^b	1.09
- e. Diffusion Coefficient Data for the Various Ferrocene Derivatives in This Study
- i. Influence of Molecular Weight on the Diffusion Coefficient



Figure S136. Correlations between the molecular weight of the ferrocene derivatives and the calculated diffusion coefficients of the neutral (blue) and oxidized (orange) species in A) DCM with 100 mM $[(nBu)_4N][B(C_6F_5)_4]$, B) DCM with 100 mM $[(nBu)_4N][PF_6]$, C) MeCN with 100 mM $[(nBu)_4N][B(C_6F_5)_4]$, D) MeCN with 100 mM $[(nBu)_4N][PF_6]$, and E) MeTHF with 100 mM $[(nBu)_4N][B(C_6F_5)_4]$ as the supporting electrolyte. The molecular weight of the counter anions was omitted for simplification purposes.

ii. Effect of Moisture on Diffusion Coefficients

Using the solution of ferrocene (2 mM) with $[(nBu)_4N][PF_6]$ (100mM) in acetonitrile, we studied the effect of moisture on the diffusion coefficient. First, the solution was made inside of the glovebox and subsequently brought outside. Under an argon flow, variable scan rate CV measurements were made. Then, nanopure water was added in increments and the same variable scan rate CV measurements were performed. The diffusion coefficient was again calculated for the brief exposure to the outside atmosphere and each subsequent addition of water. It was observed that upon the introduction of moisture into the solution, the diffusion coefficient increased, as shown in **Table S15**.

Solution	$\mathbf{D}_{\mathbf{Anodic}}$ $(\mathbf{cm}^2.\mathbf{s}^{-1})$	$\mathbf{D}_{Cathodic}$ $(\mathrm{cm}^2.\mathrm{s}^{-1})$
$Fc + [(nBu)_4N][PF_6]$ inside glove box	1.37×10^{-5}	1.33 × 10 ⁻⁵
$Fc + [(nBu)_4N][PF_6]$ brief outside exposure	1.57×10^{-5}	1.64 × 10 ⁻⁵
$Fc + [(nBu)_4N][PF_6]$ outside + 25 µL n.p. H ₂ O	1.77×10^{-5}	1.95 × 10 ⁻⁵
Fc + $[(nBu)_4N][PF_6]$ + 75 µL n.p. H ₂ O	2.08×10^{-5}	2.22×10^{-5}

Table S15. Diffusion coefficient values for a ferrocene (2mM) and $[(nBu)_4N][PF_6]$ (100mM) solution upon increase of the water content under an Ar blanket.

4. Additional Characterization Data



Figure S137. ¹H-NMR spectrum of $[Ag(MeCN)_4][B(C_6F_5)_4]$ recorded in acetone- d_6 (500 MHz) at room temperature with an internal toluene standard. Quantification of the coordinating acetonitrile molecules was possible with the addition of 1 equivalent of toluene to the silver(I) salt NMR solution, as well as the use of the acetonitrile-CH₃ satellite peak (1/200th of the main acetonitrile signal) and its ratio to the toluene-CH₃ signal (i.e., four acetonitrile molecules per toluene molecule; 4:1).



Figure S139. IR spectra comparison between $[(nBu)_4N]Cl$ (dotted line) and $[(nBu)_4N][B(C_6F_5)_4]$ (solid line).



Figure S140. ¹H-NMR spectrum of $[(nBu)_4N][B(C_6F_5)_4]$ recorded in acetone- d_6 (500 MHz) at room temperature.



Figure S141. ¹⁹F-NMR spectrum of [(*n*Bu)₄N][B(C₆F₅)₄] recorded in acetone-*d*₆ (470 MHz) at room temperature.

5. References

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