Chemical and Electrochemical Properties of [Cp*Rh] Complexes Supported by a Hybrid Phosphine-Pyridine Ligand

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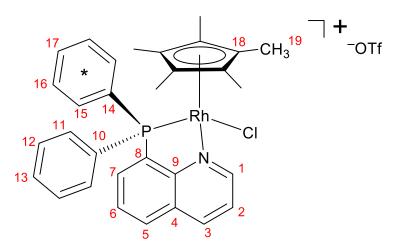


Figure S1. Numbering scheme for assignment of NMR data for complex 1-Cl (* in ring denotes phenyl group closest to Cp* ring).

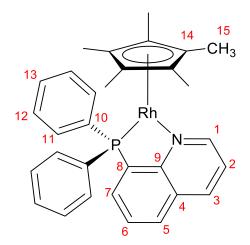


Figure S2. Numbering scheme for assignment of NMR data for complex 2.

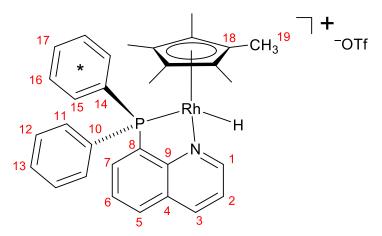


Figure S3. Numbering scheme for assignment of NMR data for complex **3** (* in ring denotes phenyl group closest to Cp* ring).

0.0 0	

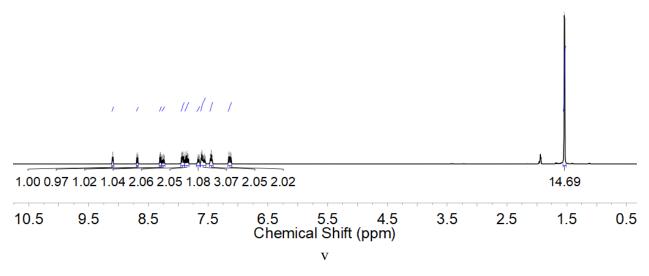


Figure S4. ¹H NMR spectrum (500 MHz, CD₃CN) of 1-Cl.

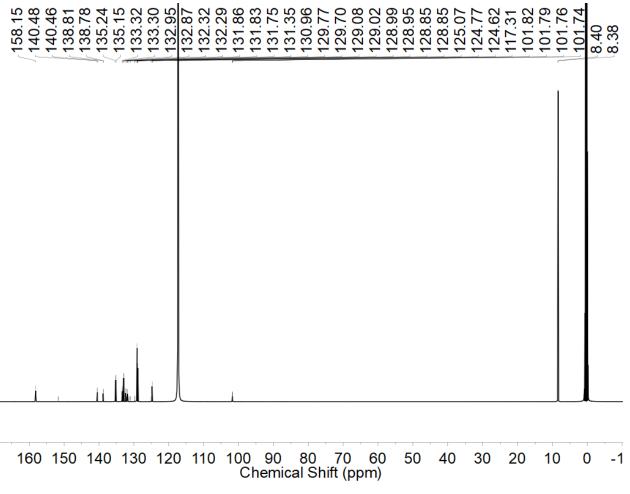
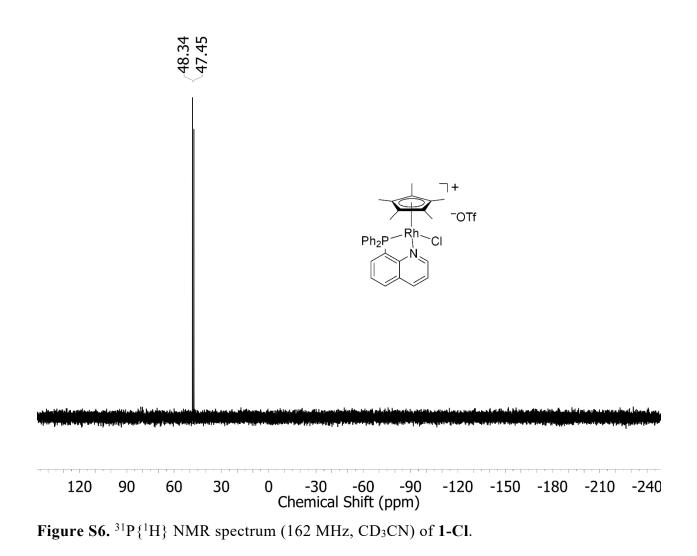


Figure S5. ${}^{13}C{}^{1}H$ NMR spectrum (126 MHz, CD₃CN) of 1-Cl.



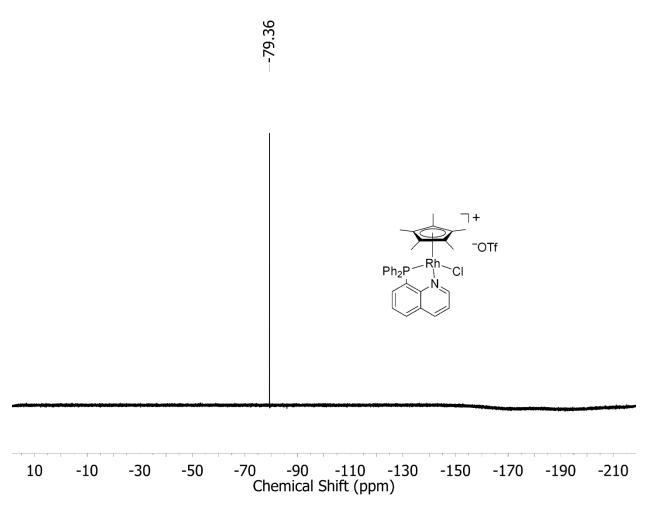


Figure S7. ¹⁹F NMR spectrum (376 MHz, CD₃CN) of 1-Cl.

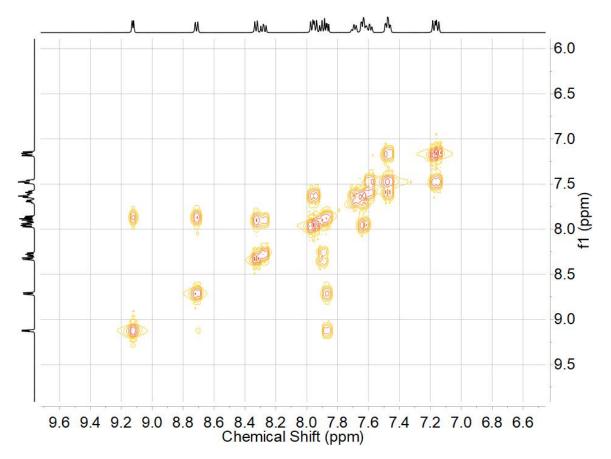


Figure S8. COSY NMR spectrum (CD₃CN) of 1-Cl.

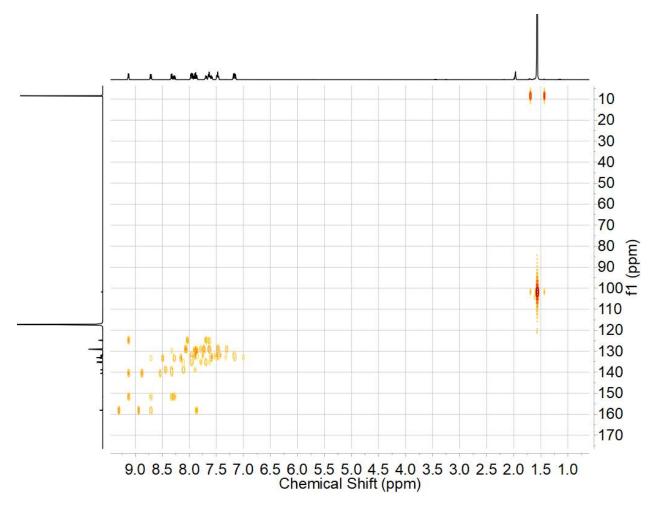


Figure S9. HMBC NMR spectrum (CD₃CN) of 1-Cl.

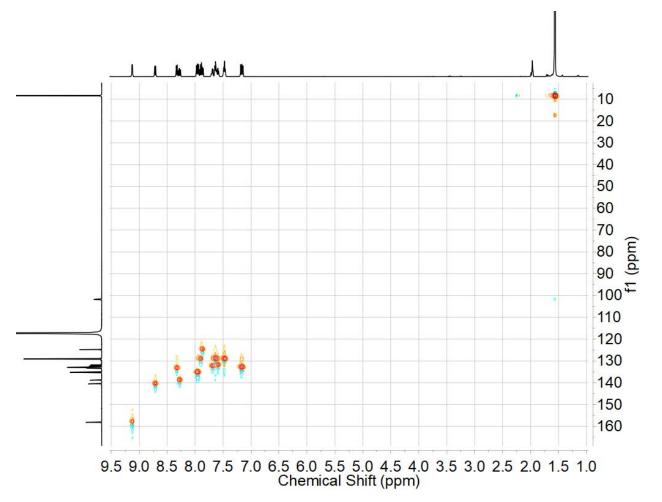


Figure S10. HSQC NMR spectrum (CD₃CN) of 1-Cl.

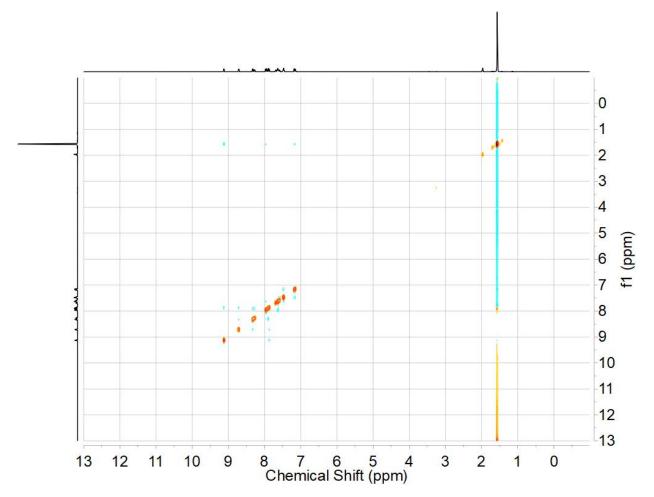


Figure S11. NOESY NMR spectrum (CD₃CN) of 1-Cl.

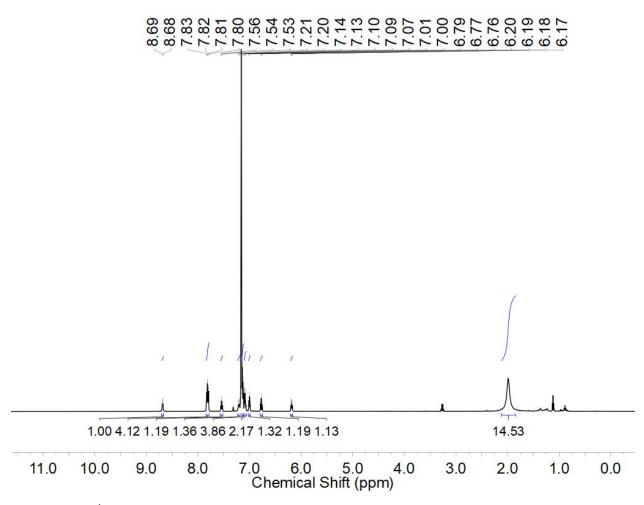


Figure S12. ¹H NMR spectrum (500 MHz, C_6D_6) of 2.

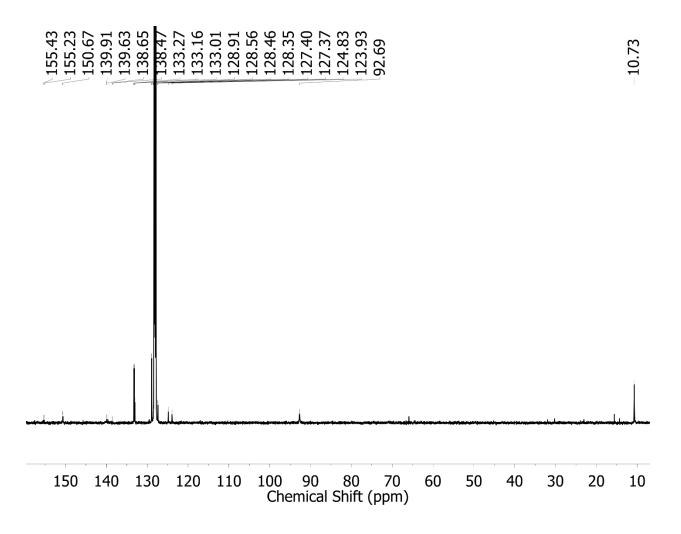


Figure S13. ${}^{13}C{}^{1}H$ NMR spectrum (126 MHz, C₆D₆) of 2.

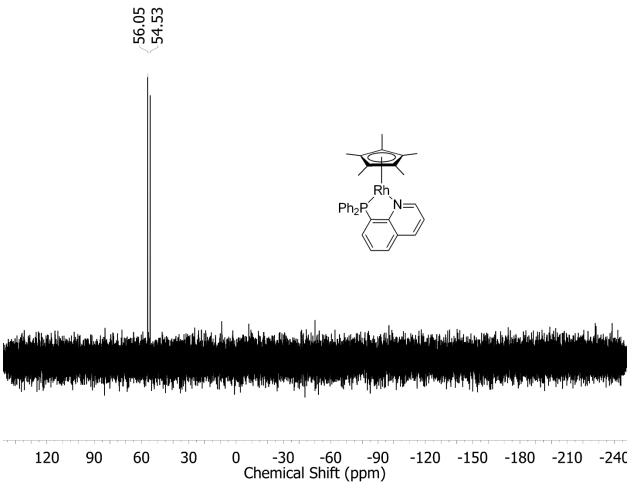


Figure S14. ${}^{31}P{}^{1}H$ NMR spectrum (162 MHz, C₆D₆) of 2.

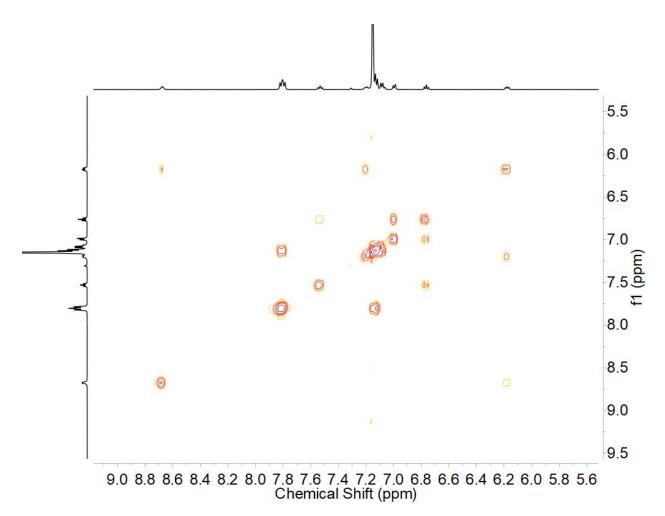


Figure S15. COSY NMR spectrum (C₆D₆) of 2.

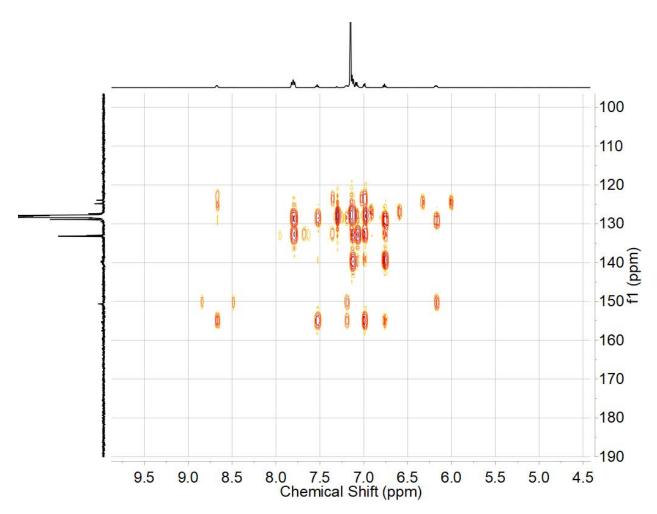


Figure S16. HMBC NMR spectrum (C_6D_6) of 2.

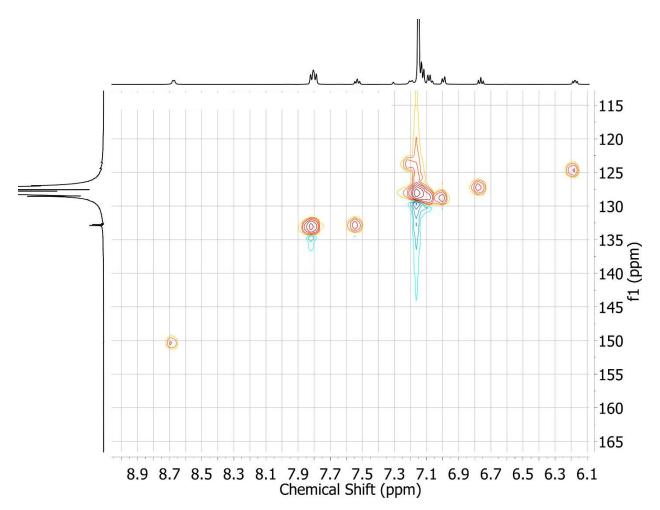


Figure S17. HSQC NMR spectrum (C₆D₆) of 2.

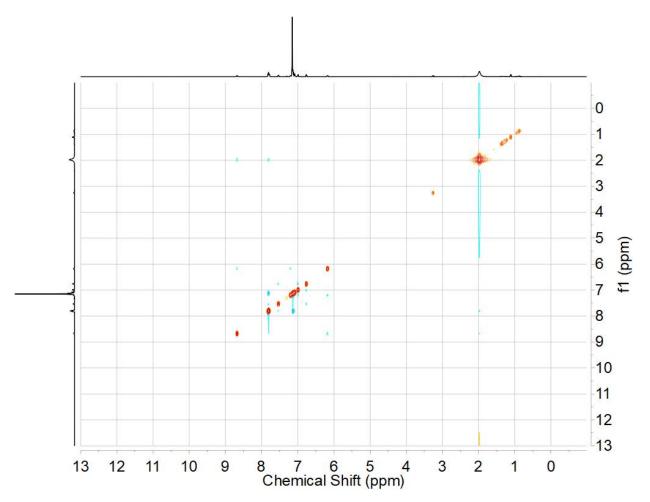


Figure S18. NOESY NMR spectrum (C₆D₆) of 2.



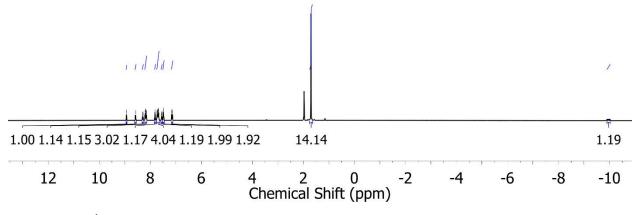


Figure S19. ¹H NMR spectrum (400 MHz, CD₃CN) of 3.

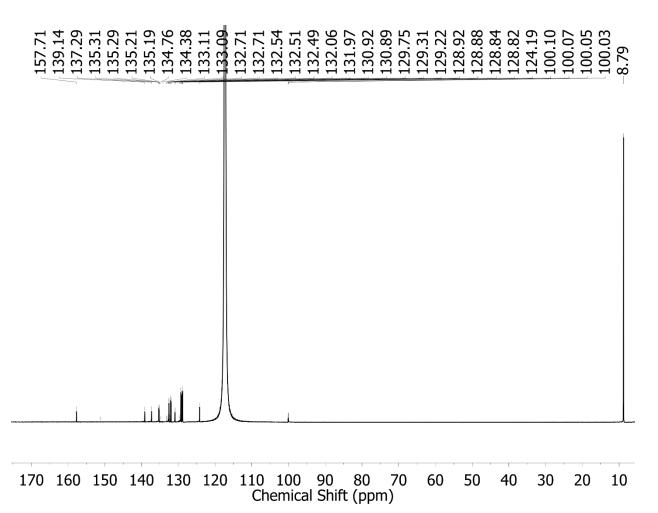


Figure S20. ${}^{13}C{}^{1}H$ NMR spectrum (126 MHz, CD₃CN) of 3.

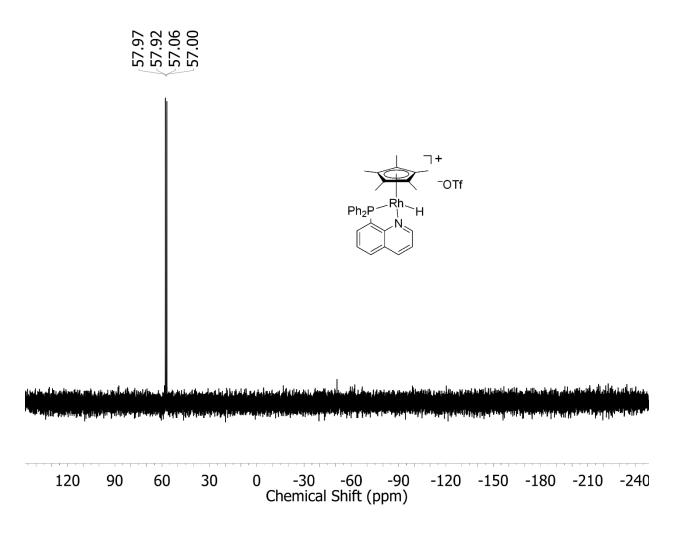


Figure S21. ${}^{31}P{}^{1}H$ NMR spectrum (162 MHz, CD₃CN) of 3.

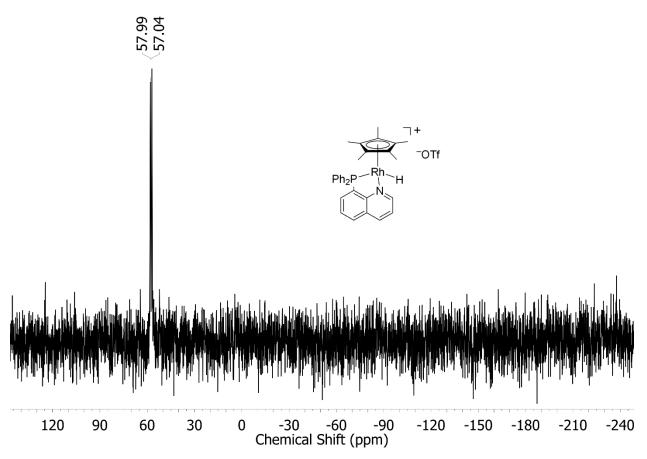


Figure S22. ³¹P NMR spectrum (162 MHz, CD₃CN) of **3**. ² $J_{P,H}$ is not observed, while ¹ $J_{P,Rh}$ of 158 Hz is observed.

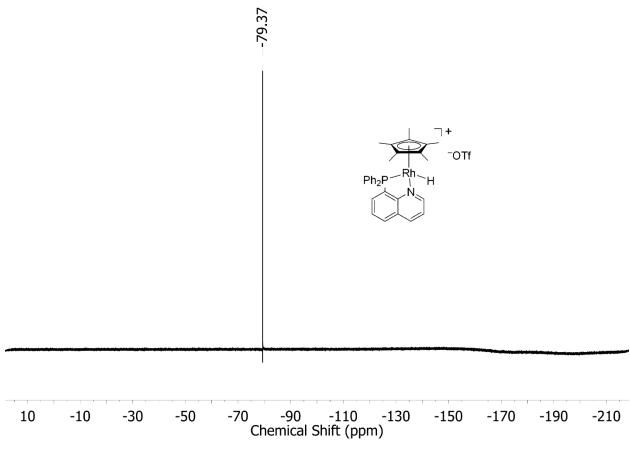


Figure S23. ¹⁹F NMR spectrum (376 MHz, CD₃CN) of 3.

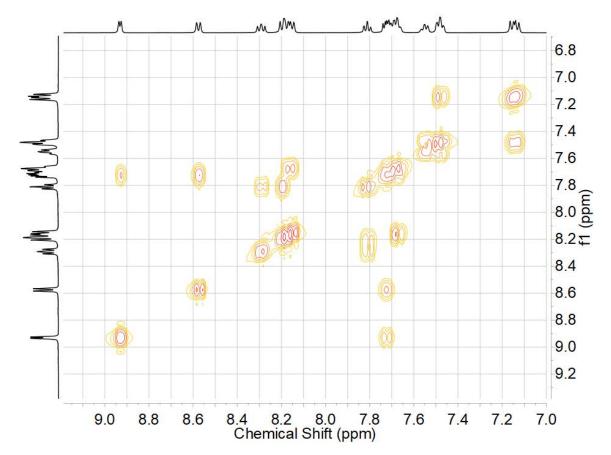


Figure S24. COSY NMR spectrum (CD₃CN) of 3.

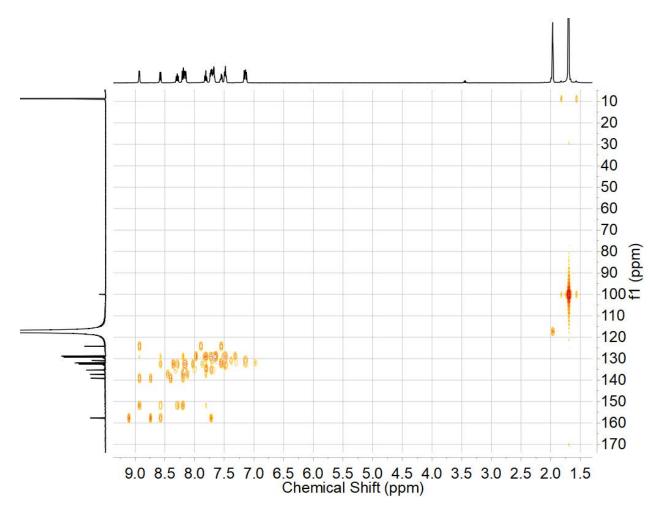


Figure S25. HMBC NMR spectrum (CD₃CN) of 3.

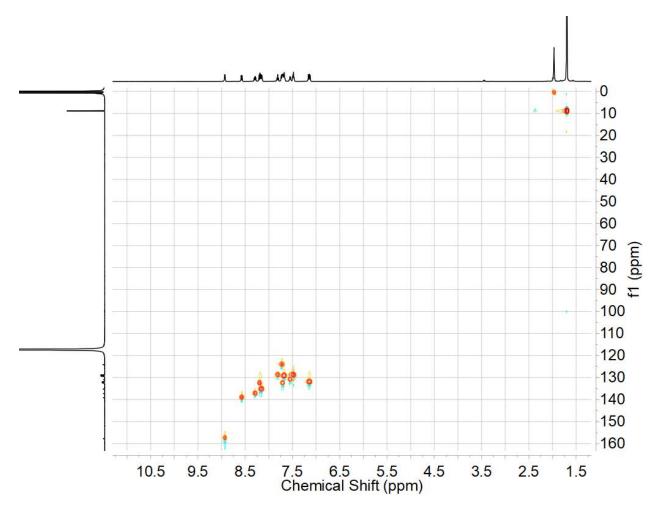


Figure S26. HSQC NMR spectrum (CD₃CN) of 3.

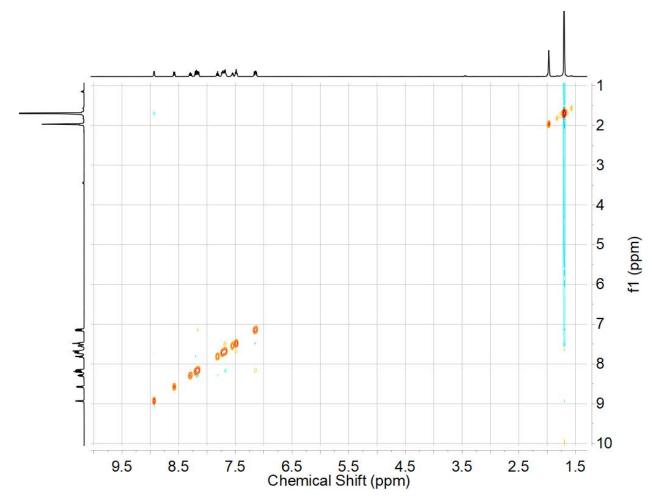


Figure S27. NOESY NMR spectrum (CD₃CN) of 3.

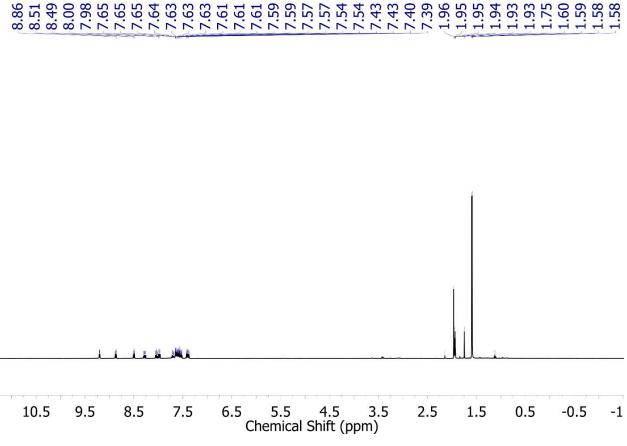


Figure S28. ¹H NMR spectrum (400 MHz, CD₃CN) of 1-NCCH₃.

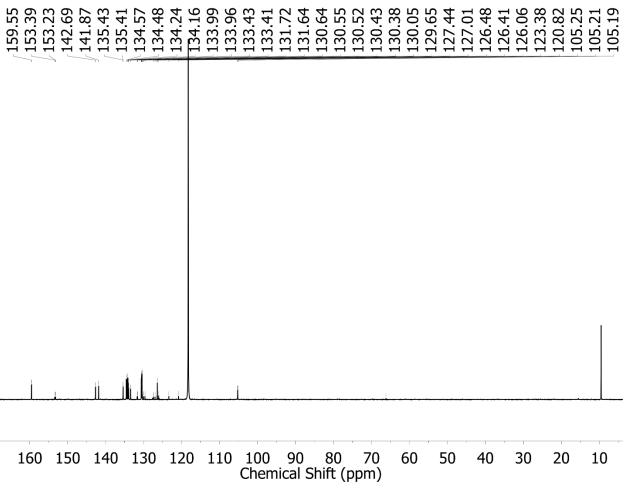


Figure S29. ¹³C NMR spectrum (162 MHz, CD₃CN) of 1-NCCH₃.

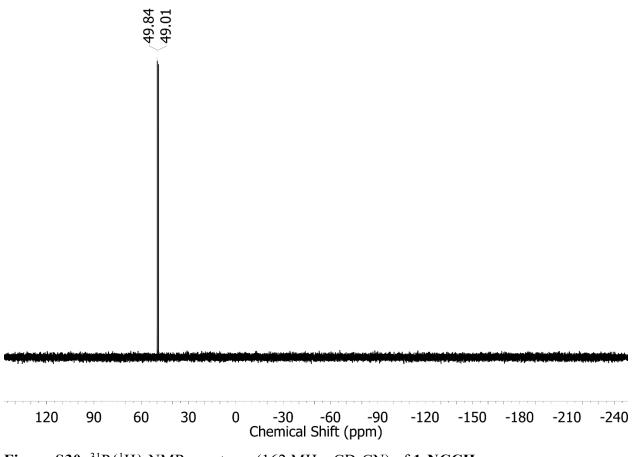


Figure S30. ${}^{31}P{}^{1}H$ NMR spectrum (162 MHz, CD₃CN) of 1-NCCH₃.

			1 1 .								I I
10	-10	-30	-50	-70 Ch	-90 emical	-110 Shift (pp	-130)m)	-150	-170	-190	-210

--79.30

Figure S31. ¹⁹F NMR spectrum (162 MHz, CD₃CN) of 1-NCCH₃.

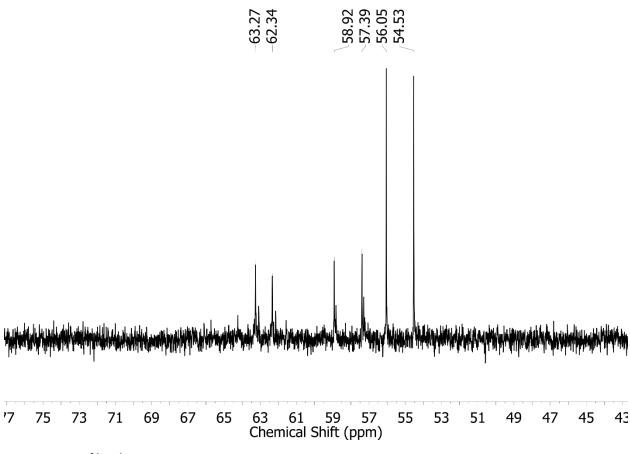


Figure S32. ³¹P{¹H} NMR spectrum (162 MHz, C_6D_6) of aliquot from chemical reduction of **3** with decamethylcobalacene.

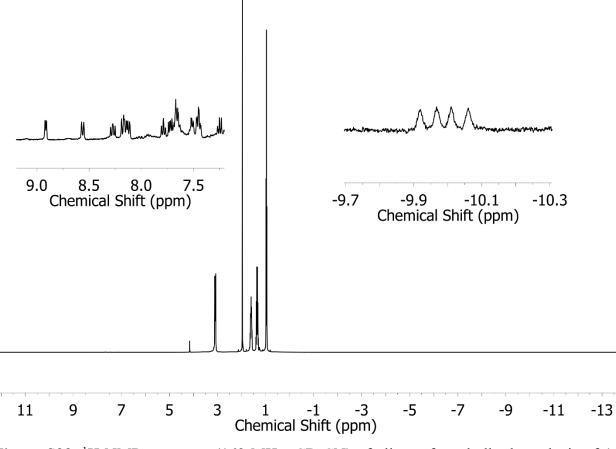


Figure S33. ¹H NMR spectrum (162 MHz, CD₃CN) of aliquot from bulk electrolysis of **1-NCCH₃** with 10 equiv. of Et₃NH⁺OTf⁻.

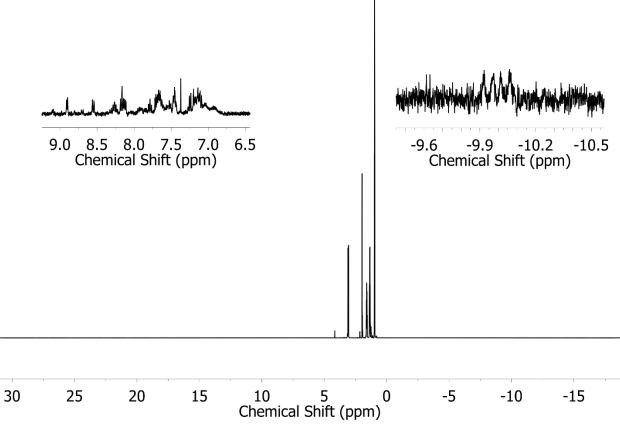


Figure S34. ¹H NMR spectrum (162 MHz, CD₃CN) of aliquot from bulk electrolysis of **1- Cl** with 10 equiv. of Et₃NH⁺OTf⁻.

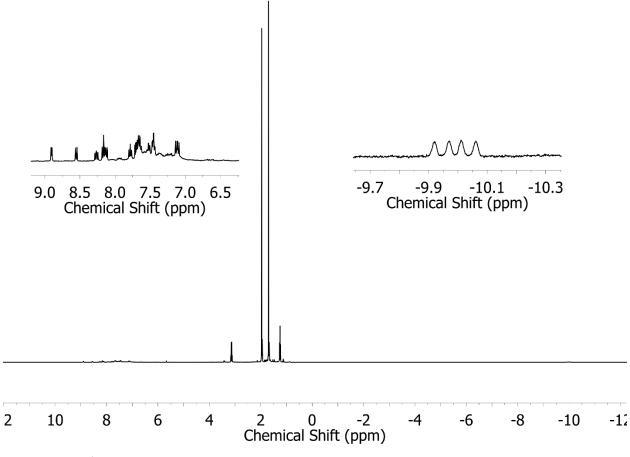


Figure S35. ¹H NMR spectrum (162 MHz, CD₃CN) of aliquot from chemical reduction of **3** with 1 equiv. of Et₃NH⁺OTf⁻ and decamethylcobaltacene.

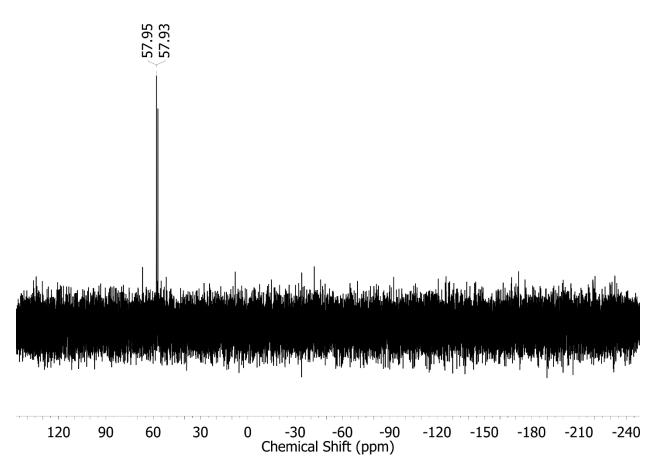


Figure S36. ³¹P{¹H} NMR spectrum (162 MHz, CD₃CN) of aliquot from chemical reduction of **3** with 1 equiv. of $Et_3NH^+OTf^-$ and decamethylcobaltacene.

UV-Vis

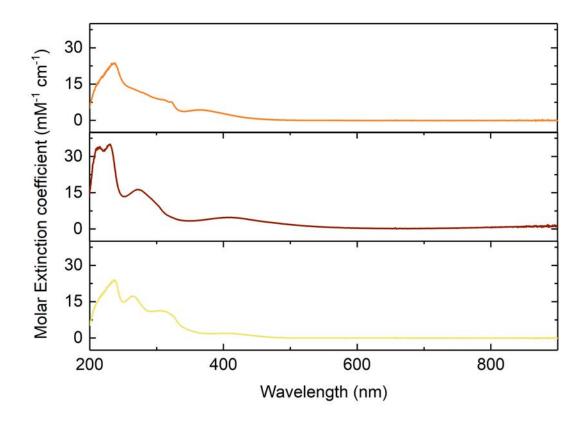


Figure S37. Electronic absorption spectra of 1-Cl (upper panel), 2 (middle panel), and 3 (lower panel) in CH₃CN.

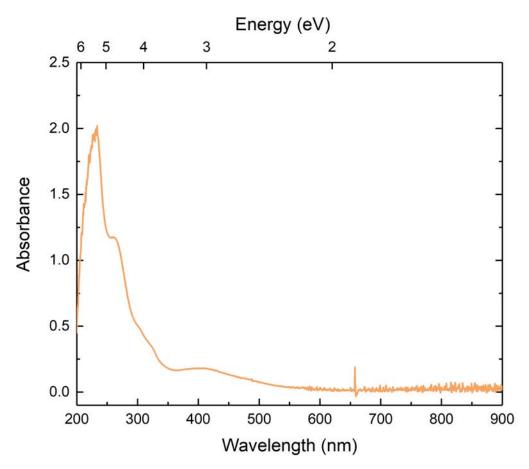


Figure S38. Electronic absorption spectrum of aliquot (CH₃CN) from bulk electrolysis of 3.

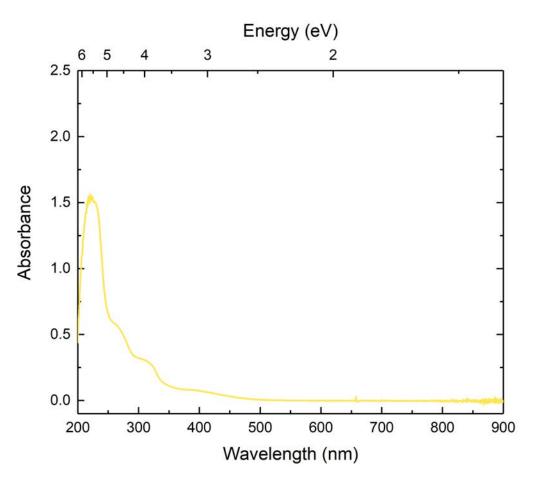


Figure S39. Electronic absorption spectrum of aliquot (CH₃CN) from bulk electrolysis of for **1-NCCH₃** with 10 equiv. of Et₃NH⁺OTf⁻.

Electrochemistry

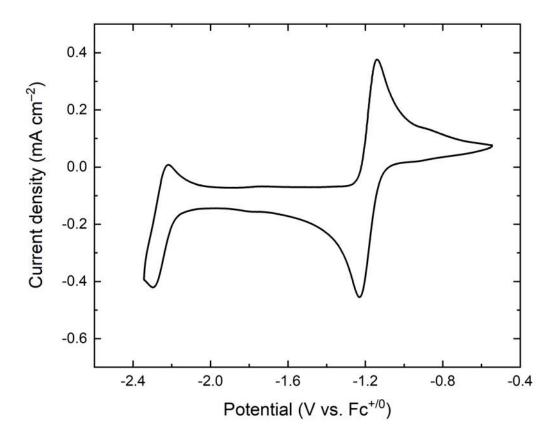


Figure S40. Cyclic voltammetry of 1-Cl (CH₃CN, 0.1 M [ⁿBu₄N][PF₆], 100 mV/s)

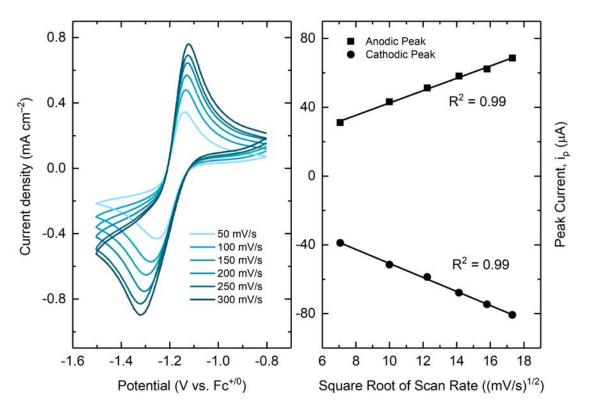


Figure S41. Left: cyclic voltammetry of first reduction event **1-Cl** at varying scan rate in CH₃CN (0.1 M [$^{n}Bu_{4}N$][PF₆]). Right: linear dependence of peak cathodic current on square root of scan rate with the y-intercept set to 0.

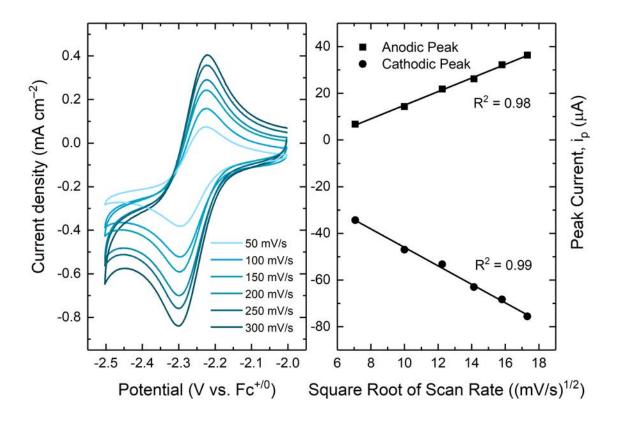


Figure S42. Left: cyclic voltammetry of second reduction event 1-Cl at varying scan rate in CH_3CN (0.1 M [nBu_4N][PF₆]). Right: linear dependence of peak cathodic current on square root of scan rate.

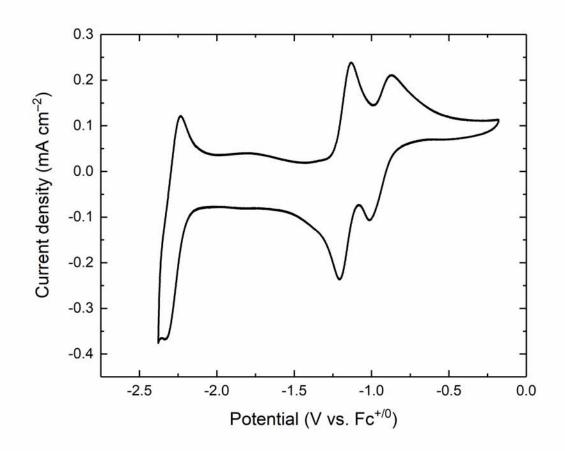


Figure S43. Cyclic voltammetry of 1-NCCH₃ (CH₃CN, 0.1 M [ⁿBu₄N][PF₆], 100 mV/s).

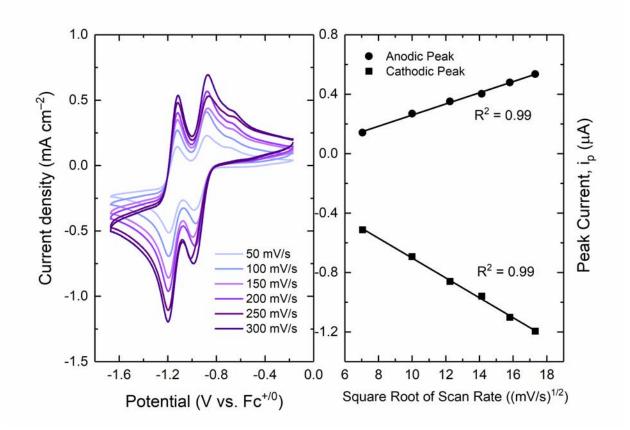


Figure S44. Left: cyclic voltammetry of second reduction event **1-NCCH**₃ at varying scan rate in CH₃CN (0.1 M [${}^{n}Bu_{4}N$][PF₆]). Right: linear dependence of peak cathodic current on square root of scan rate.

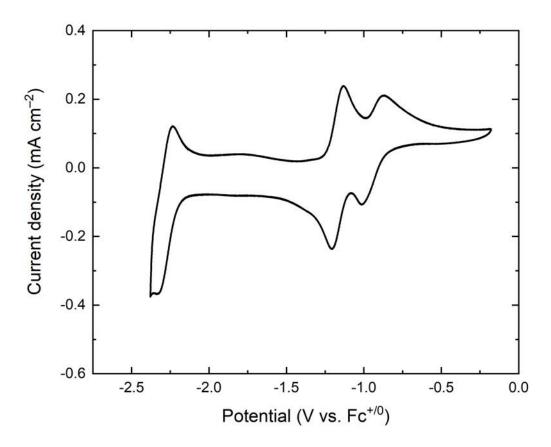


Figure S45. Cyclic voltammetry of 2 (CH₃CN, 0.1 M [ⁿBu₄N][PF₆], 100 mV/s)

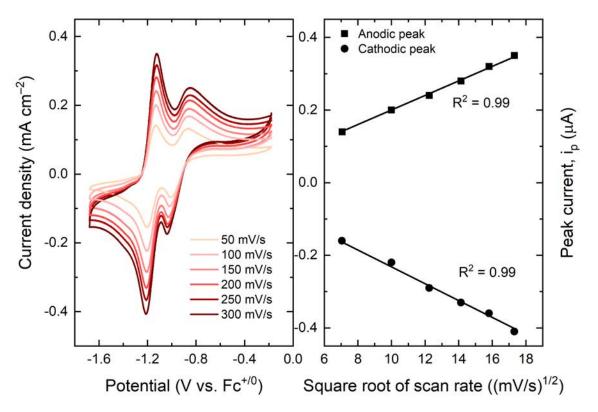


Figure S46. Left: cyclic voltammetry of **2** at varying scan rate in CH₃CN (0.1 M $[^{n}Bu_{4}N][PF_{6}]$). Right: linear dependence of peak cathodic current on square root of scan rate with the y-intercept set to 0.

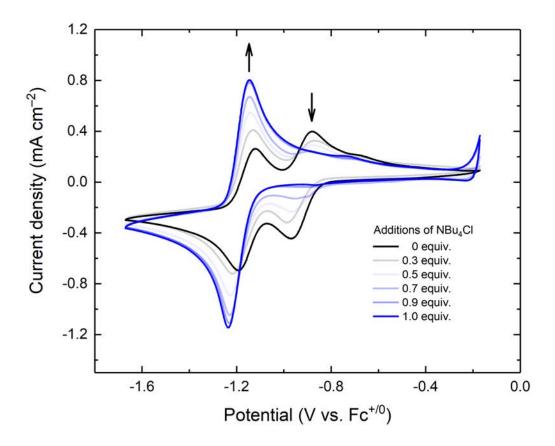


Figure S47. Titration of **1-NCCH**₃ [ⁿBu₄N][PF₆] solution with increasing equivalents of [ⁿBu₄N][Cl] (CH₃CN, 0.1 M [ⁿBu₄N][PF₆], 100 mV/s).

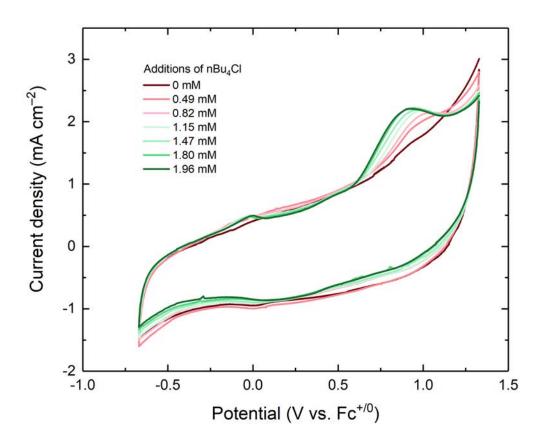


Figure S48. Titration of blank 0.1M [ⁿBu₄N][PF₆] solution with increasing equivalents of [ⁿBu₄N][Cl] (CH₃CN, 0.1 M [ⁿBu₄N][PF₆], 100 mV/s).

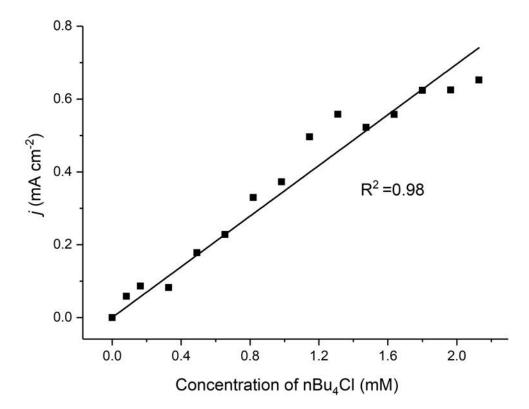


Figure S49. Linear regression of i_{pa} vs. concentration of [ⁿBu₄N][Cl]. Titration of blank 0.1M [ⁿBu₄N][PF₆] solution with increasing equivalents of [ⁿBu₄N][Cl] (CH₃CN, 0.1 M [ⁿBu₄N][PF₆], 100 mV/s).

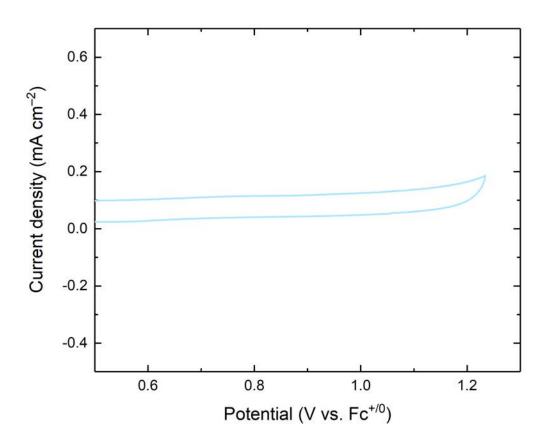


Figure S50. CV of chloride oxidation region of 2 (CH₃CN, 0.1 M [ⁿBu₄N][PF₆], 100 mV/s).

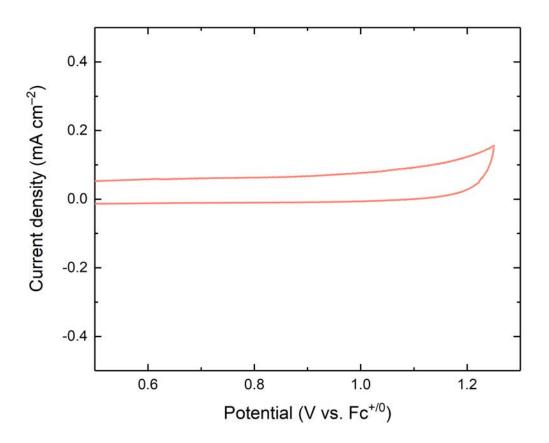


Figure S51. CV of chloride oxidation region of **1-NCCH₃** (CH₃CN, 0.1 M [ⁿBu₄N][PF₆], 100 mV/s).

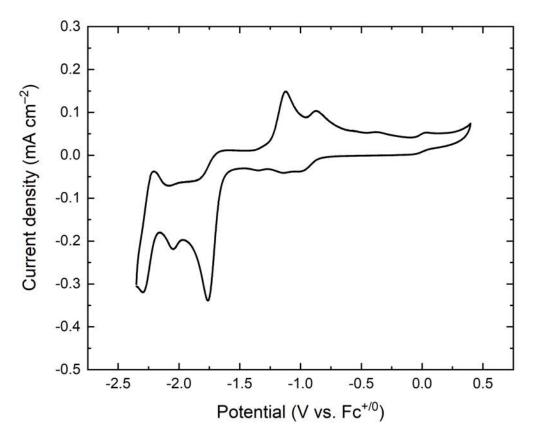


Figure S52. Cyclic voltammetry of 3 (CH₃CN, 0.1 M [ⁿBu₄N][PF₆], 100 mV/s)

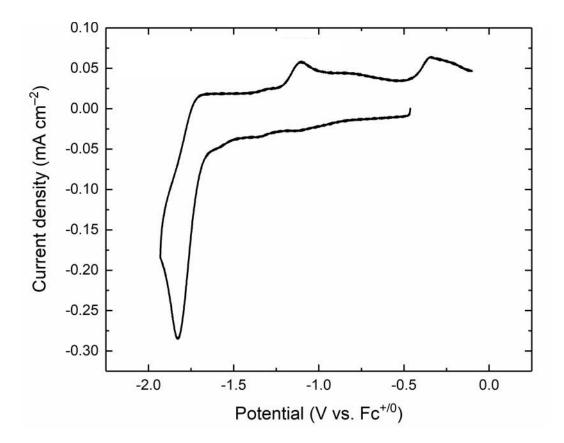


Figure S53. Cyclic voltammetry of 3 (CH₃CN, 0.1 M [ⁿBu₄N][PF₆], 4000 mV/s).

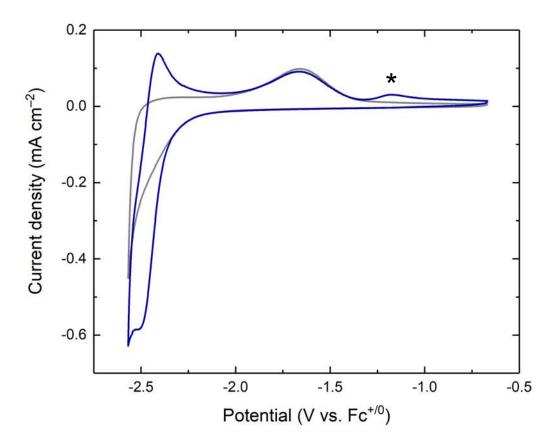


Figure S54. Cyclic voltammetry of PQN (CH₃CN, 0.1 M [ⁿBu₄N][PF₆], 100 mV/s) (*) denotes an anodic, electrode-based process resulting from cathodic scanning to rather negative potentials.

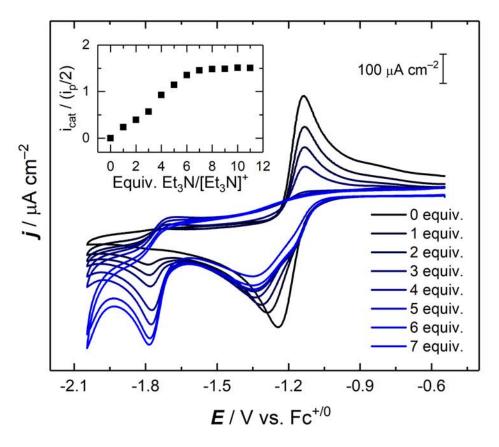


Figure S55. Cyclic voltammetry of **1-Cl** with 1 equv. of $[Et_3NH]^+/Et_3N$ in 50µL additions (CH₃CN, 0.1 M [ⁿBu₄N][PF₆], 100 mV/s). (Inset): Plot of $i_{cat}/(i_{p/2})$ vs equivalents (mMol) of $[Et_3NH]^+/Et_3N$ added.

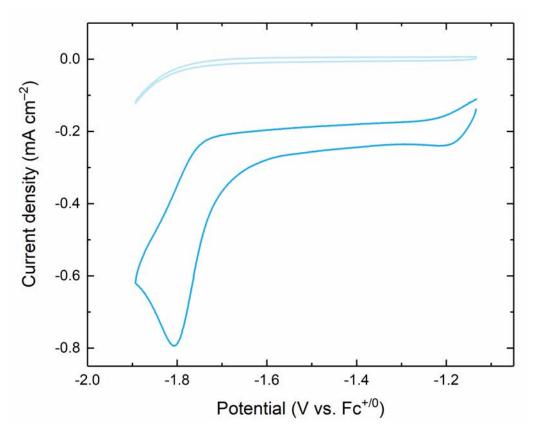


Figure S56. Cyclic voltammetry of $Et_3NH^+OTf^-$ (top); 1-Cl and 1 equiv. of $Et_3NH^+OTf^-$ (bottom) (CH₃CN, 0.1 M [ⁿBu₄N][PF₆], 100 mV/s).

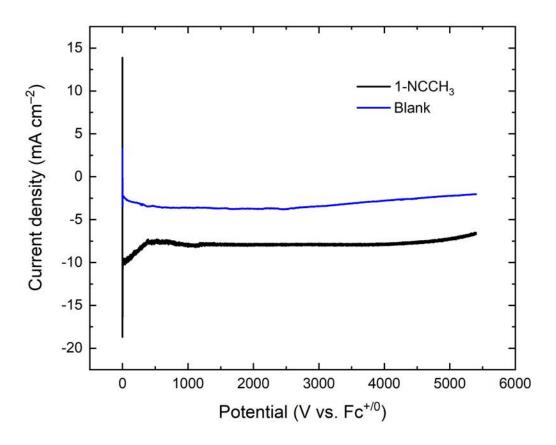


Figure S57. Chronoamperometry experiments conducted during bulk electrolyses with 1 mM **1-NCCH₃** plus acid (black line) and an acid-only blank (blue line). Polarization at -1.75 V vs Fc^{+/0}. Ten equivalents of ferrocene included as sacrificial reductant, and 10 equivalents of [Et₃NH]Br added as the acid. Supporting electrolyte was 0.1 M [ⁿBu₄N][PF₆] in each case.

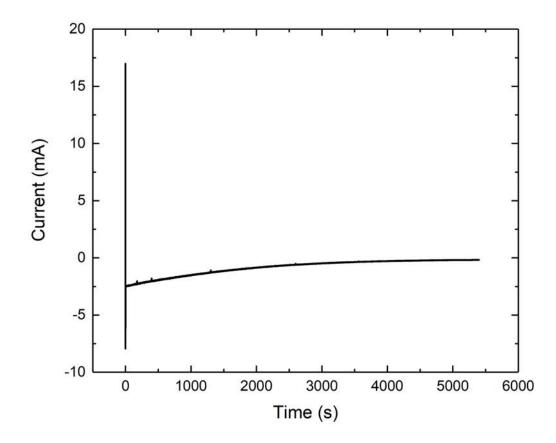


Figure S58. Bulk electrolysis data for 3 polarized at -1.75 V (CH₃CN, 0.1 M [ⁿBu₄N][PF₆]).

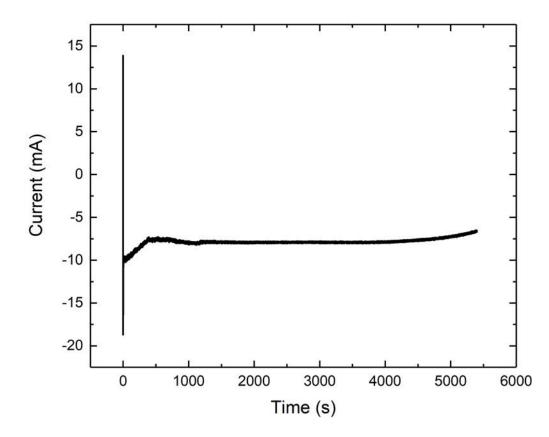


Figure S59. Bulk electrolysis data for **1-NCCH₃** with 10 equiv. of Et₃NH⁺OTf⁻ polarized at -1.75 V (CH₃CN, 0.1 M [ⁿBu₄N][PF₆], 100 mV/s).

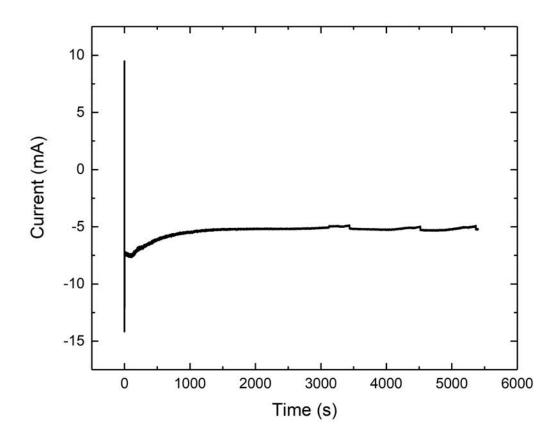


Figure S60. Bulk electrolysis data for **1-Cl** with 10 equiv. of Et₃NH⁺OTf⁻ polarized at -1.75 V (CH₃CN, 0.1 M [ⁿBu₄N][PF₆], 100 mV/s).

X-ray crystallography

Refinement Details for 1-Cl, 2 and 3.

Sets of diffraction data [16617 (1-Cl), 25594 (2) and 17776 (3) reflections using 1°-wide ω - or ϕ -scan frames with scan times of 4-6 seconds (1-Cl), 5 seconds (2) or 4-6 seconds (3)] were collected¹ for single-domain crystals of 1-Cl, 2, and 3 using monochromated Cu K α radiation (λ =1.54178 Å) on a Bruker Proteum Single Crystal Diffraction System with dual CCD detectors and associated Helios high-brilliance multilayer optics and a shared Bruker MicroSTAR microfocus Cu rotating anode x-ray source operating at 45 kV and 60 mA. Data for both compounds were collected with an Apex II CCD detector. The integrated data were corrected empirically for variable absorption effects using equivalent reflections.² The Bruker software package SHELXTL was used to solve both structures using "direct methods" techniques.³ All stages of weighted full-matrix least-squares refinement were conducted using F_o² data using the Olex software package⁴ equipped with SHELXTL XL v2014.⁵ Final crystallographic details are summarized in Table S1.

In the structure of 3, the Rh-bound hydride ligand (H41) was located as residual electron density in the Fourier difference map; it was therefore included in the model as an isotropic atom and its position was freely refined.

	1-Cl	2	3
CCDC number	1858635	1858633	1858634
Empirical formula	C ₃₂ H ₃₁ ClF ₃ NO ₃ PRhS	C ₃₁ H ₃₁ NPRh	C32H32F3NO3PRhS
Formula weight	735.97	551.45	701.52
Temperature	199.99	296.15	199.99
Wavelength	1.54178	1.54178	0.71073
Crystal system	monoclinic	monoclinic	triclinic
Space group	$P2_1/n$	$P2_1/n$	P-1
a	12.9399(2) Å	9.0754(2) Å	10.5485(9) Å
b	15.7672(3) Å	17.3941(4) Å	10.5301(9) Å
С	15.3994(3) Å	16.7425(4) Å	14.8517(12) Å
a	90	90	70.4770(10)
β	94.0144(6)	101.7270(10)	76.8720(10)
γ	90	90	82.9990(10)
Volume	3134.17(10) Å ³	2587.78(10) Å ³	1512.3(2) Å ³
Ζ	4	4	2
Density (calculated)	1.560 g/cm^3	1.415 g/cm^3	1.541 g/cm^3
Absorption coefficient	6.747 mm ⁻¹	6.053 mm ⁻¹	0.739 mm ⁻¹
F(000)	1496.0	1136.0	716.0
Crystal size	$\begin{array}{c} 0.14 \times 0.085 \times 0.045 \\ mm^3 \end{array}$	$0.17\times 0.085\times 0.03$ mm ³	$\begin{array}{c} 0.24 \times 0.23 \times 0.08 \\ mm^3 \end{array}$
Theta range	8.036 to 140.37	7.41 to 140.456	3.97 to 61.508
Index ranges	$-14 \le h \le 15, -18 \le k$ $\le 18, -15 \le l \le 18$	$\begin{array}{l} -10 \leq h \leq 8, \ -20 \leq k \\ \leq 21, \ -20 \leq l \leq 18 \end{array}$	$-14 \le h \le 15, -14 \le k \le 15, -21 \le l \le 21$
Reflections collected	16617	25594	17776
Independent reflections	$\begin{array}{l} 5720 \; [R_{int} = 0.0311, \\ R_{sigma} = 0.0311] \end{array}$	$\begin{array}{l} 4692 \; [R_{int} = 0.0276, \\ R_{sigma} = 0.0208] \end{array}$	$\begin{array}{l} 8957 \; [R_{int} = 0.0380] \\ R_{sigma} = 0.0681] \end{array}$
Absorption correction	Multi-scan	Multi-scan	Multi-scan
Max. and min. transmission	0.7533, 0.5664	0.839, 0.426	0.943, 0.842

Table S1. Crystal and Refinement Data for $[Cp*Rh(QPN)(Cl)]^+[OTf]$ (1-Cl), [Cp*Rh(QPN)] (2) and $[Cp*Rh(QPN)(H)]^+[OTf]$ (3).

Refinement method	Full-matrix least- squares on F ²	Full-matrix least- squares on F ²	Full-matrix least- squares on F ²		
Data / restraints / parameters	5720/0/393	4692/0/313	8957/0/452		
Goodness-of-fit on F^2	1.072	1.094	0.914		
Final R indices [I>2 σ (I)]	$R_1 = 0.0325,$	$R_1 = 0.0212,$	$R_1 = 0.0466,$		
R indices (all data)	$wR_2 = 0.0837$ $R_1 = 0.0342$, $wR_2 = 0.0852$	$wR_2 = 0.0536$ $R_1 = 0.0217$, $wR_2 = 0.0539$	$wR_2 = 0.1251$ $R_1 = 0.0728$, $wR_2 = 0.1485$		
Largest diff. peak and hole	$1.24 \text{ and } -0.76 \text{ e}^{-}/\text{Å}^{3}$	$0.30 \text{ and } -0.41 \text{ e}^{-}/\text{Å}^{3}$	$1.35/-0.98 \text{ e}^{-}/\text{Å}^{3}$		
${}^{a} R1 \Sigma F_{o} - F_{c} / \Sigma F_{o} \qquad {}^{b} wR2 = \left[\Sigma \left[w(F_{o}^{2} - F_{c}^{2})^{2} \right] / \Sigma \left[w(F_{o}^{2})^{2} \right] \right]^{1/2}$					

Table S2. Selected Bond Lengths for 1-Cl, 2 and 3.

Bond	1-Cl	2	3
Rh–Cl	2.3784(9)		—
Rh–P	2.260(9)	2.1744(4)	2.2486(8)
Rh–N	2.140(3)	2.0294(13)	2.093(3)
Rh–Cp*	1.830	1.917	1.862
Rh–H41			1.48(4)

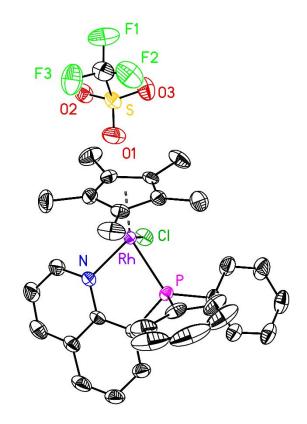


Figure S61. Full solid-state structure of 1-Cl. Hydrogen atoms omitted for clarity. Displacement ellipsoids shown at the 50% probability level.

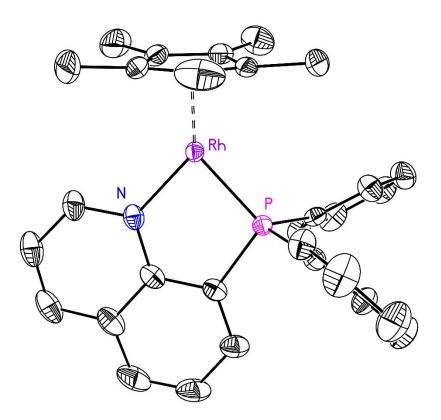


Figure S62. Full solid-state structure of **2**. Hydrogen atoms omitted for clarity. Displacement ellipsoids shown at the 50% probability level.

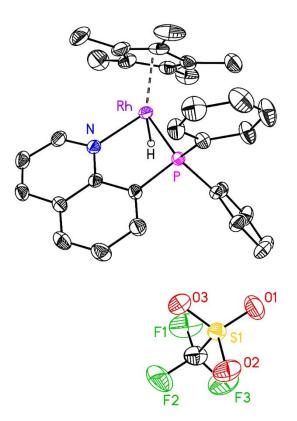


Figure S63. Full solid-state structure of **3**. Hydrogen atoms except for H41 omitted for clarity. Displacement ellipsoids shown at the 50% probability level.

References

1. APEX2, Version 2 User Manual, M86-E01078,. Bruker Analytical X-ray Systems: Madison, WI, June 2006.

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5. Sheldrick, G., Crystal structure refinement with SHELXL. Acta Crystallogr., Sect. C: Cryst. Struct. Commun. 2015, 71, 3-8.