Supporting Information for:

# 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 $\mathbf{3}$ (* in ring denotes phenyl group closest to Cp * ring).

## NMR Spectra

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Figure S4. ${ }^{1} \mathrm{H}$ NMR spectrum $\left(500 \mathrm{MHz}, \mathrm{CD}_{3} \mathrm{CN}\right)$ of $\mathbf{1 - C l}$.


Figure S5. ${ }^{13} \mathrm{C}\left\{{ }^{1} \mathrm{H}\right\}$ NMR spectrum $\left(126 \mathrm{MHz}, \mathrm{CD}_{3} \mathrm{CN}\right)$ of $\mathbf{1 - C l}$.


Figure S6. ${ }^{31} \mathrm{P}\left\{{ }^{1} \mathrm{H}\right\}$ NMR spectrum ( $162 \mathrm{MHz}, \mathrm{CD}_{3} \mathrm{CN}$ ) of 1-Cl.


Figure S7. ${ }^{19} \mathrm{~F}$ NMR spectrum ( $376 \mathrm{MHz}, \mathrm{CD}_{3} \mathrm{CN}$ ) of $\mathbf{1 - C l}$.


Figure S8. COSY NMR spectrum $\left(\mathrm{CD}_{3} \mathrm{CN}\right)$ of 1-Cl.


Figure S9. HMBC NMR spectrum $\left(\mathrm{CD}_{3} \mathrm{CN}\right)$ of 1-Cl.


Figure S10. HSQC NMR spectrum $\left(\mathrm{CD}_{3} \mathrm{CN}\right)$ of 1-Cl.


Figure S11. NOESY NMR spectrum $\left(\mathrm{CD}_{3} \mathrm{CN}\right)$ of $\mathbf{1 - C l}$.


Figure S12. ${ }^{1} \mathrm{H}$ NMR spectrum ( $500 \mathrm{MHz}, \mathrm{C}_{6} \mathrm{D}_{6}$ ) of $\mathbf{2}$.


Figure S13. ${ }^{13} \mathrm{C}\left\{{ }^{1} \mathrm{H}\right\}$ NMR spectrum $\left(126 \mathrm{MHz}, \mathrm{C}_{6} \mathrm{D}_{6}\right)$ of $\mathbf{2}$.


Figure S14. ${ }^{31} \mathrm{P}\left\{{ }^{1} \mathrm{H}\right\}$ NMR spectrum $\left(162 \mathrm{MHz}, \mathrm{C}_{6} \mathrm{D}_{6}\right)$ of $\mathbf{2}$.


Figure $\mathbf{S 1 5}$. COSY NMR spectrum $\left(\mathrm{C}_{6} \mathrm{D}_{6}\right)$ of $\mathbf{2}$.


Figure S16. HMBC NMR spectrum $\left(\mathrm{C}_{6} \mathrm{D}_{6}\right)$ of $\mathbf{2}$.


Figure $\mathbf{S 1 7}$. HSQC NMR spectrum $\left(\mathrm{C}_{6} \mathrm{D}_{6}\right)$ of $\mathbf{2}$.


Figure S18. NOESY NMR spectrum $\left(\mathrm{C}_{6} \mathrm{D}_{6}\right)$ of $\mathbf{2}$.




Figure S19. ${ }^{1} \mathrm{H}$ NMR spectrum ( $400 \mathrm{MHz}, \mathrm{CD}_{3} \mathrm{CN}$ ) of $\mathbf{3}$.


Figure S20. ${ }^{13} \mathrm{C}\left\{{ }^{1} \mathrm{H}\right\}$ NMR spectrum $\left(126 \mathrm{MHz}, \mathrm{CD}_{3} \mathrm{CN}\right)$ of $\mathbf{3}$.


Figure S21. ${ }^{31} \mathrm{P}\left\{{ }^{1} \mathrm{H}\right\}$ NMR spectrum $\left(162 \mathrm{MHz}, \mathrm{CD}_{3} \mathrm{CN}\right)$ of $\mathbf{3}$.


Figure S22. ${ }^{31} \mathrm{P}$ NMR spectrum ( $162 \mathrm{MHz}, \mathrm{CD}_{3} \mathrm{CN}$ ) of 3. ${ }^{2} J_{\mathrm{P}, \mathrm{H}}$ is not observed, while ${ }^{1} J_{\mathrm{P}, \mathrm{Rh}}$ of 158 Hz is observed.


Figure S23. ${ }^{19} \mathrm{~F}$ NMR spectrum ( $376 \mathrm{MHz}, \mathrm{CD}_{3} \mathrm{CN}$ ) of $\mathbf{3}$.


Figure S24. COSY NMR spectrum $\left(\mathrm{CD}_{3} \mathrm{CN}\right)$ of $\mathbf{3}$.


Figure S25. HMBC NMR spectrum $\left(\mathrm{CD}_{3} \mathrm{CN}\right)$ of $\mathbf{3}$.


Figure S26. HSQC NMR spectrum $\left(\mathrm{CD}_{3} \mathrm{CN}\right)$ of $\mathbf{3}$.


Figure S27. NOESY NMR spectrum $\left(\mathrm{CD}_{3} \mathrm{CN}\right)$ of $\mathbf{3}$.


Figure S28. ${ }^{1} \mathrm{H}$ NMR spectrum $\left(400 \mathrm{MHz}, \mathrm{CD}_{3} \mathrm{CN}\right)$ of $\mathbf{1}-\mathrm{NCCH}_{3}$.


Figure S29. ${ }^{13} \mathrm{C}$ NMR spectrum $\left(162 \mathrm{MHz}, \mathrm{CD}_{3} \mathrm{CN}\right)$ of $\mathbf{1}-\mathbf{N C C H}_{3}$.


Figure S30. ${ }^{31} \mathrm{P}\left\{{ }^{1} \mathrm{H}\right\}$ NMR spectrum $\left(162 \mathrm{MHz}, \mathrm{CD}_{3} \mathrm{CN}\right)$ of $\mathbf{1}-\mathbf{N C C H}_{3}$.

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Figure S31. ${ }^{19} \mathrm{~F}$ NMR spectrum $\left(162 \mathrm{MHz}, \mathrm{CD}_{3} \mathrm{CN}\right)$ of $\mathbf{1 - \mathbf { N C C H } _ { \mathbf { 3 } }}$.


Figure S32. ${ }^{31} \mathrm{P}\left\{{ }^{1} \mathrm{H}\right\}$ NMR spectrum $\left(162 \mathrm{MHz}, \mathrm{C}_{6} \mathrm{D}_{6}\right)$ of aliquot from chemical reduction of 3 with decamethylcobalacene.


Figure S33. ${ }^{1} \mathrm{H}$ NMR spectrum ( $162 \mathrm{MHz}, \mathrm{CD}_{3} \mathrm{CN}$ ) of aliquot from bulk electrolysis of $\mathbf{1 -}$ $\mathbf{N C C H}_{3}$ with 10 equiv. of $\mathrm{Et}_{3} \mathrm{NH}^{+} \mathrm{OTf}^{-}$.


Figure S34. ${ }^{1} \mathrm{H}$ NMR spectrum ( $162 \mathrm{MHz}, \mathrm{CD}_{3} \mathrm{CN}$ ) of aliquot from bulk electrolysis of $\mathbf{1 -} \mathbf{C l}$ with 10 equiv. of $\mathrm{Et}_{3} \mathrm{NH}^{+} \mathrm{OTf}^{-}$.


Figure S35. ${ }^{1} \mathrm{H}$ NMR spectrum ( $162 \mathrm{MHz}, \mathrm{CD}_{3} \mathrm{CN}$ ) of aliquot from chemical reduction of $\mathbf{3}$ with 1 equiv. of $\mathrm{Et}_{3} \mathrm{NH}^{+} \mathrm{OTf}^{-}$and decamethylcobaltacene.


Figure S36. ${ }^{31} \mathrm{P}\left\{{ }^{1} \mathrm{H}\right\}$ NMR spectrum ( $162 \mathrm{MHz}, \mathrm{CD}_{3} \mathrm{CN}$ ) of aliquot from chemical reduction of $\mathbf{3}$ with 1 equiv. of $\mathrm{Et}_{3} \mathrm{NH}^{+} \mathrm{OTf}^{-}$and decamethylcobaltacene.


Figure S37. Electronic absorption spectra of 1-Cl (upper panel), 2 (middle panel), and 3 (lower panel) in $\mathrm{CH}_{3} \mathrm{CN}$.


Figure S38. Electronic absorption spectrum of aliquot $\left(\mathrm{CH}_{3} \mathrm{CN}\right)$ from bulk electrolysis of $\mathbf{3}$.


Figure S39. Electronic absorption spectrum of aliquot $\left(\mathrm{CH}_{3} \mathrm{CN}\right)$ from bulk electrolysis of for $\mathbf{1}-\mathrm{NCCH}_{3}$ with 10 equiv. of $\mathrm{Et}_{3} \mathrm{NH}^{+} \mathrm{OTf}^{-}$.

## Electrochemistry



Figure S40. Cyclic voltammetry of $\mathbf{1 - C l}\left(\mathrm{CH}_{3} \mathrm{CN}, 0.1 \mathrm{M}\left[{ }^{\mathrm{n}} \mathrm{Bu}_{4} \mathrm{~N}\right]\left[\mathrm{PF}_{6}\right], 100 \mathrm{mV} / \mathrm{s}\right)$


Figure S41. Left: cyclic voltammetry of first reduction event $\mathbf{1 - C l}$ at varying scan rate in $\mathrm{CH}_{3} \mathrm{CN}\left(0.1 \mathrm{M}\left[{ }^{\mathrm{n}} \mathrm{Bu}_{4} \mathrm{~N}\right]\left[\mathrm{PF}_{6}\right]\right)$. 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 $\mathbf{1 - C l}$ at varying scan rate in $\mathrm{CH}_{3} \mathrm{CN}\left(0.1 \mathrm{M}\left[{ }^{\mathrm{n}} \mathrm{Bu}_{4} \mathrm{~N}\right]\left[\mathrm{PF}_{6}\right]\right)$. Right: linear dependence of peak cathodic current on square root of scan rate.


Figure S43. Cyclic voltammetry of $\mathbf{1 -} \mathbf{N C C H}_{3}\left(\mathrm{CH}_{3} \mathrm{CN}, 0.1 \mathrm{M}\left[{ }^{\mathrm{n}} \mathrm{Bu}_{4} \mathrm{~N}\right]\left[\mathrm{PF}_{6}\right], 100 \mathrm{mV} / \mathrm{s}\right)$.


Figure S44. Left: cyclic voltammetry of second reduction event $\mathbf{1 - \mathbf { N C C H } _ { 3 }}$ at varying scan rate in $\mathrm{CH}_{3} \mathrm{CN}\left(0.1 \mathrm{M}\left[{ }^{\mathrm{n}} \mathrm{Bu}_{4} \mathrm{~N}\right]\left[\mathrm{PF}_{6}\right]\right)$. Right: linear dependence of peak cathodic current on square root of scan rate.


Figure S45. Cyclic voltammetry of $\mathbf{2}\left(\mathrm{CH}_{3} \mathrm{CN}, 0.1 \mathrm{M}\left[{ }^{\mathrm{n}} \mathrm{Bu}_{4} \mathrm{~N}\right]\left[\mathrm{PF}_{6}\right], 100 \mathrm{mV} / \mathrm{s}\right)$


Figure S46. Left: cyclic voltammetry of 2 at varying scan rate in $\mathrm{CH}_{3} \mathrm{CN}(0.1 \mathrm{M}$ [ $\left.{ }^{\mathrm{B}} \mathrm{Bu}_{4} \mathrm{~N}\right]\left[\mathrm{PF}_{6}\right]$ ). Right: linear dependence of peak cathodic current on square root of scan rate with the $y$-intercept set to 0 .


Figure S47. Titration of $\mathbf{1 -} \mathbf{N C C H}_{3}\left[{ }^{\mathrm{n}} \mathrm{Bu}_{4} \mathrm{~N}\right]\left[\mathrm{PF}_{6}\right]$ solution with increasing equivalents of [ $\left.{ }^{\mathrm{B}} \mathrm{Bu}_{4} \mathrm{~N}\right][\mathrm{Cl}]\left(\mathrm{CH}_{3} \mathrm{CN}, 0.1 \mathrm{M}\left[{ }^{\mathrm{n}} \mathrm{Bu}_{4} \mathrm{~N}\right]\left[\mathrm{PF}_{6}\right], 100 \mathrm{mV} / \mathrm{s}\right)$.


Figure S48. Titration of blank $0.1 \mathrm{M}\left[{ }^{[ } \mathrm{Bu}_{4} \mathrm{~N}\right]\left[\mathrm{PF}_{6}\right]$ solution with increasing equivalents of $\left[{ }^{\mathrm{n}} \mathrm{Bu}_{4} \mathrm{~N}\right][\mathrm{Cl}]\left(\mathrm{CH}_{3} \mathrm{CN}, 0.1 \mathrm{M}\left[{ }^{\mathrm{n}} \mathrm{Bu}_{4} \mathrm{~N}\right]\left[\mathrm{PF}_{6}\right], 100 \mathrm{mV} / \mathrm{s}\right)$.


Figure S49. Linear regression of $i_{p a} v s$. concentration of [ $\left.{ }^{n} \mathrm{Bu}_{4} \mathrm{~N}\right][\mathrm{Cl}]$. Titration of blank 0.1 M [ $\left.{ }^{\mathrm{B}} \mathrm{Bu}_{4} \mathrm{~N}\right]\left[\mathrm{PF}_{6}\right]$ solution with increasing equivalents of $\left[{ }^{\mathrm{n}} \mathrm{Bu}{ }_{4} \mathrm{~N}\right][\mathrm{Cl}]\left(\mathrm{CH}_{3} \mathrm{CN}, 0.1 \mathrm{M}\right.$ [ $\left.{ }^{\mathrm{n}} \mathrm{Bu}_{4} \mathrm{~N}\right]\left[\mathrm{PF}_{6}\right], 100 \mathrm{mV} / \mathrm{s}$ ).


Figure S50. CV of chloride oxidation region of $2\left(\mathrm{CH}_{3} \mathrm{CN}, 0.1 \mathrm{M}\left[{ }^{\mathrm{n}} \mathrm{Bu}_{4} \mathrm{~N}\right]\left[\mathrm{PF}_{6}\right], 100 \mathrm{mV} / \mathrm{s}\right)$.


Figure S51. CV of chloride oxidation region of $\mathbf{1 - N C C H} 3\left(\mathrm{CH}_{3} \mathrm{CN}, 0.1 \mathrm{M}\left[{ }^{\mathrm{n}} \mathrm{Bu}_{4} \mathrm{~N}\right]\left[\mathrm{PF}_{6}\right], 100\right.$ $\mathrm{mV} / \mathrm{s}$ ).


Figure S52. Cyclic voltammetry of $\mathbf{3}\left(\mathrm{CH}_{3} \mathrm{CN}, 0.1 \mathrm{M}\left[{ }^{\mathrm{n}} \mathrm{Bu}_{4} \mathrm{~N}\right]\left[\mathrm{PF}_{6}\right], 100 \mathrm{mV} / \mathrm{s}\right)$


Figure S53. Cyclic voltammetry of $\mathbf{3}\left(\mathrm{CH}_{3} \mathrm{CN}, 0.1 \mathrm{M}\left[{ }^{\mathrm{n}} \mathrm{Bu}_{4} \mathrm{~N}\right]\left[\mathrm{PF}_{6}\right], 4000 \mathrm{mV} / \mathrm{s}\right)$.


Figure S54. Cyclic voltammetry of $\mathrm{PQN}\left(\mathrm{CH}_{3} \mathrm{CN}, 0.1 \mathrm{M}\left[{ }^{\mathrm{n}} \mathrm{Bu}_{4} \mathrm{~N}\right]\left[\mathrm{PF}_{6}\right], 100 \mathrm{mV} / \mathrm{s}\right)\left({ }^{*}\right)$ denotes an anodic, electrode-based process resulting from cathodic scanning to rather negative potentials.


Figure S55. Cyclic voltammetry of $\mathbf{1 - C l}$ with 1 equv. of $\left[\mathrm{Et}_{3} \mathrm{NH}\right]^{+} / \mathrm{Et}_{3} \mathrm{~N}$ in $50 \mu \mathrm{~L}$ additions $\left(\mathrm{CH}_{3} \mathrm{CN}, 0.1 \mathrm{M}\left[{ }^{\mathrm{n}} \mathrm{Bu}_{4} \mathrm{~N}\right]\left[\mathrm{PF}_{6}\right], 100 \mathrm{mV} / \mathrm{s}\right)$. (Inset): Plot of $\mathrm{i}_{\text {cat }} /\left(\mathrm{i}_{\mathrm{p} / 2}\right)$ vs equivalents $(\mathrm{mMol})$ of $\left[\mathrm{Et}_{3} \mathrm{NH}\right]^{+} / \mathrm{Et}_{3} \mathrm{~N}$ added.


Figure S56. Cyclic voltammetry of $\mathrm{Et}_{3} \mathrm{NH}^{+} \mathrm{OTf}^{-}$(top); $\mathbf{1 - C l}$ and 1 equiv. of $\mathrm{Et}_{3} \mathrm{NH}^{+} \mathrm{OTf}^{-}$ (bottom) $\left(\mathrm{CH}_{3} \mathrm{CN}, 0.1 \mathrm{M}\left[{ }^{\mathrm{n}} \mathrm{Bu}_{4} \mathrm{~N}\right]\left[\mathrm{PF}_{6}\right], 100 \mathrm{mV} / \mathrm{s}\right)$.


Figure S57. Chronoamperometry experiments conducted during bulk electrolyses with 1 mM $\mathbf{1 - N C C H} 3$ plus acid (black line) and an acid-only blank (blue line). Polarization at -1.75 V vs $\mathrm{Fc}^{+/ 0}$. Ten equivalents of ferrocene included as sacrificial reductant, and 10 equivalents of $\left[\mathrm{Et}_{3} \mathrm{NH}\right] \mathrm{Br}$ added as the acid. Supporting electrolyte was $0.1 \mathrm{M}\left[{ }^{\mathrm{n}} \mathrm{Bu}_{4} \mathrm{~N}\right]\left[\mathrm{PF}_{6}\right]$ in each case.


Figure S58. Bulk electrolysis data for $\mathbf{3}$ polarized at $-1.75 \mathrm{~V}\left(\mathrm{CH}_{3} \mathrm{CN}, 0.1 \mathrm{M}\left[{ }^{\mathrm{n}} \mathrm{Bu}_{4} \mathrm{~N}\right]\left[\mathrm{PF}_{6}\right]\right)$.


Figure S59. Bulk electrolysis data for $\mathbf{1 -} \mathbf{N C C H}_{3}$ with 10 equiv. of $\mathrm{Et}_{3} \mathrm{NH}^{+} \mathrm{OTf}^{-}$polarized at $-1.75 \mathrm{~V}\left(\mathrm{CH}_{3} \mathrm{CN}, 0.1 \mathrm{M}\left[{ }^{\mathrm{n}} \mathrm{Bu}_{4} \mathrm{~N}\right]\left[\mathrm{PF}_{6}\right], 100 \mathrm{mV} / \mathrm{s}\right)$.


Figure S60. Bulk electrolysis data for $\mathbf{1 - C l}$ with 10 equiv. of $\mathrm{Et}_{3} \mathrm{NH}^{+} \mathrm{OTf}^{-}$polarized at -1.75 $\mathrm{V}\left(\mathrm{CH}_{3} \mathrm{CN}, 0.1 \mathrm{M}\left[{ }^{\mathrm{n}} \mathrm{Bu}_{4} \mathrm{~N}\right]\left[\mathrm{PF}_{6}\right], 100 \mathrm{mV} / \mathrm{s}\right)$.

## 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 $1^{0}$-wide $\omega$ - or $\phi$-scan frames with scan times of 4-6 seconds (1-CI), 5 seconds (2) or 4-6 seconds (3)] were collected ${ }^{1}$ for single-domain crystals of $\mathbf{1 - C l}, \mathbf{2}$, and $\mathbf{3}$ using monochromated $\mathrm{Cu} \mathrm{K} \alpha$ radiation ( $\lambda=1.54178 \AA$ ) 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 $\mathrm{F}_{\mathrm{o}}{ }^{2}$ data using the Olex software package ${ }^{4}$ equipped with SHELXTL XL v2014. ${ }^{5}$ Final crystallographic details are summarized in Table S1.

In the structure of $\mathbf{3}$, 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.

Table S1. Crystal and Refinement Data for $[\mathrm{Cp} * \mathrm{Rh}(\mathrm{QPN})(\mathrm{Cl})]^{+}[\mathrm{OTf}](\mathbf{1 - C l}),[\mathrm{Cp} * \mathrm{Rh}(\mathrm{QPN})]$ (2) and $[\mathrm{Cp} * \mathrm{Rh}(\mathrm{QPN})(\mathrm{H})]^{+}[\mathrm{OTf}]$ (3).

|  | 1-Cl | 2 | 3 |
| :---: | :---: | :---: | :---: |
| CCDC number | 1858635 | 1858633 | 1858634 |
| Empirical formula | $\mathrm{C}_{32} \mathrm{H}_{31} \mathrm{ClF}_{3} \mathrm{NO}_{3} \mathrm{PRhS}$ | $\mathrm{C}_{31} \mathrm{H}_{31} \mathrm{NPR}$ h | $\mathrm{C}_{32} \mathrm{H}_{32} \mathrm{~F}_{3} \mathrm{NO}_{3} \mathrm{PRhS}$ |
| 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 | $\mathrm{P} 21 / \mathrm{n}$ | $\mathrm{P} 21 / \mathrm{n}$ | P-1 |
| $a$ | 12.9399(2) $\AA$ | 9.0754(2) Å | 10.5485(9) $\AA$ |
| $b$ | 15.7672(3) $\AA$ | 17.3941(4) $\AA$ | 10.5301(9) $\AA$ |
| $c$ | 15.3994(3) $\AA$ | 16.7425(4) $\AA$ | 14.8517(12) A |
| $a$ | 90 | 90 | 70.4770(10) |
| $\beta$ | 94.0144(6) | 101.7270(10) | 76.8720(10) |
| $\gamma$ | 90 | 90 | 82.9990(10) |
| Volume | $3134.17(10) \AA^{3}$ | 2587.78(10) $\AA^{3}$ | 1512.3(2) $\AA^{3}$ |
| Z | 4 | 4 | 2 |
| Density (calculated) | $1.560 \mathrm{~g} / \mathrm{cm}^{3}$ | $1.415 \mathrm{~g} / \mathrm{cm}^{3}$ | $1.541 \mathrm{~g} / \mathrm{cm}^{3}$ |
| Absorption coefficient | $6.747 \mathrm{~mm}^{-1}$ | $6.053 \mathrm{~mm}^{-1}$ | $0.739 \mathrm{~mm}^{-1}$ |
| F(000) | 1496.0 | 1136.0 | 716.0 |
| Crystal size | $\begin{gathered} 0.14 \times 0.085 \times 0.045 \\ \mathrm{~mm}^{3} \end{gathered}$ | $\begin{gathered} 0.17 \times 0.085 \times 0.03 \\ \mathrm{~mm}^{3} \end{gathered}$ | $\begin{gathered} 0.24 \times 0.23 \times 0.08 \\ \mathrm{~mm}^{3} \end{gathered}$ |
| Theta range | 8.036 to 140.37 | 7.41 to 140.456 | 3.97 to 61.508 |
| Index ranges | $\begin{gathered} -14 \leq \mathrm{h} \leq 15,-18 \leq \mathrm{k} \\ \leq 18,-15 \leq 1 \leq 18 \end{gathered}$ | $\begin{gathered} -10 \leq \mathrm{h} \leq 8,-20 \leq \mathrm{k} \\ \leq 21,-20 \leq 1 \leq 18 \end{gathered}$ | $\begin{aligned} & -14 \leq \mathrm{h} \leq 15,-14 \leq \\ & \mathrm{k} \leq 15,-21 \leq 1 \leq 21 \end{aligned}$ |
| Reflections collected | 16617 | 25594 | 17776 |
| Independent reflections | $\begin{gathered} 5720\left[\mathrm{R}_{\text {int }}=0.0311,\right. \\ \left.\mathrm{R}_{\text {sigma }}=0.0311\right] \end{gathered}$ | $\begin{gathered} 4692\left[\mathrm{R}_{\text {int }}=0.0276\right. \\ \left.\mathrm{R}_{\text {sigma }}=0.0208\right] \end{gathered}$ | $\begin{gathered} 8957\left[\mathrm{R}_{\text {int }}=0.0380\right. \\ \left.\mathrm{R}_{\text {sigma }}=0.0681\right] \end{gathered}$ |
| Absorption correction | Multi-scan | Multi-scan | Multi-scan |
| Max. and min. transmission | 0.7533, 0.5664 | 0.839, 0.426 | 0.943, 0.842 |


| Refinement method | Full-matrix leastsquares on $\mathrm{F}^{2}$ | Full-matrix leastsquares on $\mathrm{F}^{2}$ | Full-matrix leastsquares on $\mathrm{F}^{2}$ |
| :---: | :---: | :---: | :---: |
| Data / restraints / parameters | 5720/0/393 | 4692/0/313 | 8957/0/452 |
| Goodness-of-fit on $\mathrm{F}^{2}$ | 1.072 | 1.094 | 0.914 |
| Final R indices [ $\mathrm{I}>2 \sigma(\mathrm{I})$ ] | $\begin{gathered} \mathrm{R}_{1}=0.0325 \\ \mathrm{wR}_{2}=0.0837 \end{gathered}$ | $\begin{gathered} \mathrm{R}_{1}=0.0212 \\ \mathrm{wR}_{2}=0.0536 \end{gathered}$ | $\begin{gathered} \mathrm{R}_{1}=0.0466 \\ \mathrm{wR}_{2}=0.1251 \end{gathered}$ |
| R indices (all data) | $\begin{gathered} \mathrm{R}_{1}=0.0342 \\ \mathrm{wR}_{2}=0.0852 \end{gathered}$ | $\begin{gathered} \mathrm{R}_{1}=0.0217, \\ \mathrm{wR}_{2}=0.0539 \end{gathered}$ | $\begin{gathered} \mathrm{R}_{1}=0.0728, \\ \mathrm{wR}_{2}=0.1485 \end{gathered}$ |
| Largest diff. peak and hole | 1.24 and $-0.76 \mathrm{e}^{-/} \AA^{3}$ | 0.30 and $-0.41 \mathrm{e}^{-} / \AA^{3}$ | $1.35 /-0.98 \mathrm{e}^{-} / \AA^{3}$ |

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

| Bond | $\mathbf{1 - C l}$ | $\mathbf{2}$ | $\mathbf{3}$ |
| :---: | :---: | :---: | :---: |
| $\mathrm{Rh}-\mathrm{Cl}$ | $2.3784(9)$ | - | - |
| $\mathrm{Rh}-\mathrm{P}$ | $2.260(9)$ | $2.1744(4)$ | $2.2486(8)$ |
| $\mathrm{Rh}-\mathrm{N}$ | $2.140(3)$ | $2.0294(13)$ | $2.093(3)$ |
| $\mathrm{Rh}-\mathrm{Cp}^{*}$ | 1.830 | 1.917 | 1.862 |
| $\mathrm{Rh}-\mathrm{H} 41$ | - | - | $1.48(4)$ |



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 H 41 omitted for clarity. Displacement ellipsoids shown at the 50\% probability level.

## References

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