Supplementary Information for
Structure and Dynamic Behavior of Rhodium Complexes Supported by Lewis Acidic Group 13 Metallatranes

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Figure S1. Full cyclic voltammogram of 1-Cl (100 mV/s) in 0.1 M TBAPF₆ in THF referenced to the Fc/Fc⁺ redox couple. First oxidation $E_{pa} = 0.21$ V; second oxidation $E_{pa} = 1.00$ V.

Figure S2. Cyclic voltammogram of 2-Cl (100 mV/s) in 0.1 M TBAPF₆ in THF referenced to the Fc/Fc⁺ redox couple. First oxidation $E_{pa} = 0.12$ V; second oxidation $E_{pa} = 0.41$ V; third oxidation $E_{pa} = 0.65$. The return reduction at $E_{pc} = 0.81$ V is absent in the top CV, demonstrating that it is an electrochemical event not related to the first oxidation.
Figure S3. $^1$H (top) and $^1$H{${}^{31}$P} (bottom) NMR spectra of 1-Cl (400 MHz) in CD$_2$Cl$_2$ at -18°C.

Figure S4. $^1$H COSY NMR spectrum of 1-Cl (400 MHz) in C$_6$D$_5$Br at 0°C.
Figure S5. Low temperature VT $^1$H NMR spectrum of 1-Cl (400 MHz) in CD$_2$Cl$_2$. In order from bottom to top: −73°C, −49°C, −18°C, and 25°C.

Figure S6. High temperature VT $^1$H NMR spectrum of 1-Cl (400 MHz) in toluene-$d_8$. 
Figure S7. $^1$H NMR spectrum of 1-Cl (400 MHz) in C$_6$D$_5$Br at 115°C. The bad shims are an effect of the shimming coils being at an elevated temperature.

Figure S8. $^{31}$P{$^1$H} NMR spectrum of 1-Cl (162 MHz) in CD$_2$Cl$_2$ at −18°C.
Figure S9. High temperature VT $^{31}$P{\textsuperscript{1}H} NMR spectra of 1-Cl (162 MHz) in C$_6$D$_5$Br.
Figure S10. $^1$H (top) and $^{1}H^{(31P)}$ (bottom) NMR spectra of 2-Cl (400 MHz) in CD$_2$Cl$_2$ at −49°C.

Figure S11. $^1$H COSY NMR spectrum of 2-Cl (400 MHz) in C$_6$D$_5$Br at 0°C.
Figure S12. Low temperature VT $^1$H NMR spectrum of 2-Cl (400 MHz) in CD$_2$Cl$_2$.

Figure S13. High temperature VT $^1$H NMR spectrum of 2-Cl (400 MHz) in C$_6$D$_5$Br.

Figure S14. $^1$H NMR spectrum of 2-Cl (400 MHz) in C$_6$D$_5$Br at 75°C.
**Figure S15.** $^{31}$P{$^1$H} NMR spectrum of 2-Cl (162 MHz) in CD$_2$Cl$_2$ at −18°C.

**Figure S16.** High temperature VT $^{31}$P{$^1$H} NMR spectra of 2-Cl (162 MHz) in C$_6$D$_5$Br. * denote a minor impurity. Note: The average of the three peaks at -18°C: $(93.3 + 51.2 + 30.5)/3 = 58.3$ ppm, which is close to the 58.6 ppm shift observed at high temperatures.
Figure S17. $^{31}$P{$^1$H} NMR spectrum of 2-Cl (162 MHz) in C$_6$D$_5$Br at 107°C.

Figure S18. $^1$H (top) and $^1$H{$^{31}$P} (bottom) NMR spectra of 1-CH$_3$ (400 MHz) in toluene-$d_8$ at −18°C. * denotes residual THF.
Figure S19. $^1$H COSY NMR spectrum of $1$-$\text{CH}_3$ (400 MHz) in toluene-$d_8$ at $-18^\circ\text{C}$.

Figure S20. Low temperature VT $^1$H{$^31$P} NMR spectrum of $1$-$\text{CH}_3$ (400 MHz) in toluene-$d_8$. * denotes residual THF.
Figure S21. High temperature VT $^1$H NMR spectrum of 1-CH$_3$ (400 MHz) in toluene-$d_8$.

Figure S22. $^{31}$P{$^1$H} NMR spectrum of 1-CH$_3$ (162 MHz) in toluene-$d_8$ at −18°C.
Figure S23. VT $^{31}$P{${}^1$H} NMR spectra of 1-CH$_3$ (162 MHz) in toluene-$d_8$.

Figure S24. $^{31}$P{${}^1$H} NMR spectrum of 1-CH$_3$ (162 MHz) in toluene-$d_8$ at 97°C. The peaks for $P_1$ and $P_3$ have not yet coalesced at this temperature.
**Figure S25.** $^1$H (top) and $^1$H{${}^{31}$P} (bottom) NMR spectra of 2-CH$_3$ (400 MHz) in toluene-$d_8$ at $-13^\circ$C. * denotes residual THF.

**Figure S26.** $^1$H NMR spectrum of 2-CH$_3$ sample sent for elemental analysis in THF-$d_8$. Crystals of 2-CH$_3$(C$_6$H$_6$) was subjected to vacuum prior to elemental analysis (EA). The NMR of the aryl region for the EA sample shows that the relative integration of C$_6$H$_6$ to 2-CH$_3$ is 0.5 to 1.
Figure S27. $^1$H COSY NMR spectrum of 2-CH$_3$ (400 MHz) in toluene-$d_8$ at $-13^\circ$C.

Figure S28. Low temperature VT $^1$H{$^{31}$P} NMR spectrum of 2-CH$_3$ (400 MHz) in toluene-$d_8$. * denotes residual THF.

Figure S29. High temperature VT $^1$H{$^{31}$P} NMR spectrum of 2-CH$_3$ (400 MHz) in toluene-$d_8$. * denotes residual THF.
Figure S30. $^{31}$P$\{^1$H$\}$ NMR spectrum of 2-CH$_3$ (162 MHz) in toluene-$d_8$ at 3°C.

Figure S31. VT $^{31}$P$\{^1$H$\}$ NMR spectra of 2-CH$_3$ (162 MHz) in toluene-$d_8$.

Figure S32. $^{31}$P$\{^1$H$\}$ NMR spectrum of 2-CH$_3$ (162 MHz) in toluene-$d_8$ at 97°C. The peaks for $P_1$ and $P_3$ have not yet coalesced at this temperature.
**Figure S33.** $^1$H (top) and $^1$H$[^{31}\text{P}]$ (bottom) NMR spectra of 1-H (400 MHz) in CD$_2$Cl$_2$ at 25°C.

**Figure S34.** $^1$H COSY NMR spectrum of 1-H (500 MHz) in CD$_2$Cl$_2$ at 25°C.
Figure S35. Low temperature VT $^1\text{H}\{^{31}\text{P}\}$ NMR spectrum of 1-H (400 MHz) in CD$_2$Cl$_2$.

Figure S36. Low temperature VT $^1\text{H}\{^{31}\text{P}\}$ NMR spectrum of 1-H (400 MHz) in CD$_2$Cl$_2$ in hydride region. In order from bottom to top: −73°C, −49°C, −8°C and 25°C.

Figure S37. $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum of 1-H (162 MHz) in CD$_2$Cl$_2$ at −73°C.
Figure S38. VT $^{31}$P{$^1$H} NMR spectra of 1-H (162 MHz) in CD$_2$Cl$_2$.

Figure S39. $^1$H (top) and $^1$H{$^{31}$P} (bottom) NMR spectra of 2-H (400 MHz) in toluene-$d_8$ at 25°C.
Figure S40. $^1$H COSY NMR spectrum of 2-H (400 MHz) in toluene-$d_8$ at $-73^\circ$C.

Figure S41. Low temperature VT $^1$H{$^{31}$P} NMR spectrum of 2-H (400 MHz) in toluene-$d_8$.

Figure S42. Low temperature VT $^1$H{$^{31}$P} NMR spectrum of 2-H (400 MHz) in toluene-$d_8$ in hydride region.
Figure S43. High temperature VT $^1$H{$^{31}$P} NMR spectrum of 2-H (400 MHz) in toluene-$d_8$.

Figure S44. $^{31}$P{$^1$H} NMR spectrum of 2-H (162 MHz) in toluene-$d_8$ at $-49^\circ$C.
Figure S45. Low temperature VT $^{31}$P{$^1$H} NMR spectra of 2-H (162 MHz) in toluene-$d_8$. At room temperature, the only visible phosphorus signal corresponds to the phosphine trans to the hydride ligand (labeled as P$_2$ in main text). The other two phosphorus nuclei are not visible at room temperature because they are near coalescence (labeled as P$_1$ and P$_3$ in main text). At higher temperatures the two phosphines cis to the hydride are equivalent and appear as a doublet, corresponding to both P$_{1,3}$.

Figure S46. High temperature VT $^{31}$P{$^1$H} NMR spectra of 2-H (162 MHz) in toluene-$d_8$. At room temperature, the only visible phosphorus signal corresponds to the phosphine trans to the hydride ligand (labeled as P$_2$ in main text). The other two phosphorus nuclei are not visible at room temperature because they are near coalescence (labeled as P$_1$ and P$_3$ in main text). At higher temperatures the two phosphines cis to the hydride are equivalent and appear as a doublet, corresponding to both P$_{1,3}$. 
**Figure S47.** $^{31}$P{H} NMR spectrum of 2-H (162 MHz) in toluene-d$_8$ at 97°C.

**Table S1.** Calculation of approximate rate constants and energy barriers for the fluxional processes that equilibrate P$_1$ and P$_3$ for all complexes.

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<th>1-Cl</th>
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<th>1-CH3</th>
<th>2-CH3</th>
<th>1-H</th>
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<td>T$_e$ (K)</td>
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<td>345</td>
<td>&gt;370</td>
<td>&gt;370</td>
<td>265</td>
<td>279</td>
</tr>
<tr>
<td>Δ (Hz)</td>
<td>2905.7</td>
<td>3338.9</td>
<td>3493.7</td>
<td>3749.6</td>
<td>2562.8</td>
<td>2482.4</td>
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<tr>
<td>J (Hz)</td>
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<td>325</td>
<td>314</td>
<td>317</td>
<td>265</td>
<td>273</td>
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<td>$k_e$ (s$^{-1}$)</td>
<td>6681</td>
<td>7625</td>
<td>7947</td>
<td>8506</td>
<td>5873</td>
<td>5711</td>
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<td>ΔG$^\ddagger$ (kcal/mol)</td>
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<td>14.2</td>
<td>&gt;15.2</td>
<td>&gt;15.2</td>
<td>10.9</td>
<td>11.5</td>
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where $k_e = \left(\frac{\pi}{\sqrt{2}}\right) \times \left(\sqrt{\Delta v^2 + 6j^2}\right)^{\frac{1}{2}}$ for a coupled system and Eyring relationship, $\Delta G^\ddagger = RT_e[23.76 + \ln(T_e/k_e)]$.

**References**