

Supporting Information

Stability-Enhanced Hydrogen-Evolving Dirhodium Photocatalysts Through Ligand Modification

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Experimental methods

General consideration. All reactions were carried out in a N₂-filled glovebox or on a high vacuum manifold unless otherwise noted. All solvents were dried by passage through an alumina column under argon. The starting material [Rh^I(COD)Cl]₂ (COD = 1,5-cyclooctadiene) was obtained from Strem Chemicals, HCl (4 M in dioxane), and ^tBuNC were obtained from Sigma-Aldrich, whereas O₂ was purchased from Airgas. Tfe₂pma,¹ **1**, **2**, **3**,² and AdNC³ were prepared as described in the literature. Elemental analysis was performed by Midwest Microlab LLC.

Physical methods. NMR data were collected at the MIT Department of Chemistry Instrument Facility (DCIF) on a Varian Mercury 300 or Varian INOVA 500 spectrometer. NMR solvents (THF-d₈, CD₂Cl₂) were purchased from Cambridge Isotope Labs and dried over sieves prior to use. ¹H NMR spectra were referenced to residual proteo resonances of the given solvent. ³¹P{¹H} NMR spectra were referenced to an external 85% D₃PO₄ standard. UV-vis spectra were recorded at 293 K in quartz cuvettes on a Spectral Instruments 400 series diode array or Varian Cary 5000 spectrometer and blanked against the appropriate solvent. IR spectra were recorded on a PerkinElmer Spectrum 400 FT-IR/FT-FIR Spectrometer outfitted with a Pike Technologies GladiATR attenuated total reflectance accessory with a monolithic diamond crystal stage and pressure clamp. Samples were suspended in Nujol® for all IR measurements. Photochemical reactions were performed using a 1000 W high-pressure Hg/Xe arc lamp (Oriel) and the beam was passed through a water-jacketed filter holder containing appropriate long pass filters, an iris and collimating lens.

Synthesis of Rh₂^{0,II}(tfe₂pma)₂(CNAd)₂Cl₂ (4**).** To a saturated CH₂Cl₂ solution of [Rh^I(COD)Cl]₂ (157 mg, 0.318 mmol) was added tfe₂pma (309.6 mg, 0.6356 mmol, 2.00 equiv) to effect an immediate color change from yellow to dark brown/yellow. Addition of AdNC (102.5 mg, 0.6357 mmol, 2.00 equiv) in CH₂Cl₂ afforded a red solution that faded to orange over the course of 5 min. The solution was allowed to stir for 10 h during which time an orange solid formed. The mixture was concentrated to dryness, suspended in a mixture of 1 mL CH₂Cl₂/15 mL hexanes and allowed to settle. The supernatant was removed and the solid dried under vacuum to yield 453 mg (90.6%) of Rh₂(tfe₂pma)₂(AdNC)₂Cl₂ as a yellow powder. ¹H NMR (300 MHz, CD₂Cl₂) δ/ppm: 4.40–5.09 (br, m, 16H), 2.87 (pseudoquintet, 6H), 2.10 (br, m, 6H), 1.96 (br, m, 6H), 1.90 (br, m, 6H), 1.67 (br, m, 12H). ³¹P{¹H} NMR (121.5 MHz, CD₂Cl₂) δ/ppm: 145.1 (m, 2P), 124.5 (m, 2P).

(1) T. S. Teets, T. R. Cook, and D. G. Nocera, *Inorg. Synth.* 2010, **35**, 164.

(2) T. S. Teets, T. R. Cook, B. D. McCarthy, and D. G. Nocera, *J. Am. Chem. Soc.* 2011, **133**, 8114.

(3) T. Sasaki, A. Nakanishi, and M. Ohno, *J. Org. Chem.* 1981, **46**, 5445.

IR: $\tilde{\nu}_{\text{CN}} = 2126, 2157 \text{ cm}^{-1}$. Elem. Anal.: Calcd. for $\text{C}_{40}\text{H}_{52}\text{Cl}_2\text{F}_{24}\text{N}_4\text{O}_8\text{P}_4\text{Rh}_2$: C, 30.53; H, 3.33; N, 3.56. Found: C, 30.49; H, 3.29; N, 3.37.

Preparation of $\text{Rh}_2^{\text{II,II}}(\text{tfepma})_2(\text{CNAd})_2\text{Cl}_3\text{H}$ (5). A J-Young NMR tube was charged with a 0.7 mL THF- d_8 solution of **4** (25 mg, 0.016 mmol) and freeze pumped thaw degassed on a high vacuum manifold. $\text{HCl}_{(\text{g})}$ (25 equiv) was generated by adding 2 mL of sulfuric acid to anhydrous NaCl (23 mg) and vacuum transferred to the NMR tube and three additional FPT cycles were executed. Two isomers are obtained (~6:1 ratio). Major isomer: ^1H NMR (300 MHz, THF- d_8) δ/ppm : 5.51–4.35 (br, m, 16H), 2.95 (pseudoquintet, 6H), 2.11 (br, m, 18H), 1.65 (br, m, 12H), -14.57 (dt, $^1J_{\text{Rh-H}} = 13.5 \text{ Hz}$ and $^2J_{\text{P-H}} = 9.2 \text{ Hz}$, Rh-H, 1H). $^{31}\text{P}\{^1\text{H}\}$ NMR (121.5 MHz, THF- d_8) δ/ppm : 138.1 (m, 2P), 116.7 (m, 2P). Minor isomer: ^1H NMR (300 MHz, THF- d_8) δ/ppm : ~5.51–~4.35 (br, m, 16H, overlapped with major isomer), 3.00 (pseudoquintet, 6H), 2.21–2.09 (br, m, 18H, overlapped with major isomer), 1.69 (br, m, 12H, overlapped with major isomer), -18.93 (dt (apparent quartet), $^1J_{\text{Rh-H}} = ^2J_{\text{P-H}} = 15.3 \text{ Hz}$, Rh-H, 1H). $^{31}\text{P}\{^1\text{H}\}$ NMR (121.5 MHz, THF- d_8) δ/ppm : 132.3 (m, 2P), ~116.1 (m, 2P, overlapped with major isomer).

Synthesis of $\text{Rh}_2^{\text{II,II}}(\text{tfepma})_2(\text{CNAd})_2\text{Cl}_2$ (6). A solution of **4** (50.0 mg, 0.0318 mmol) in 0.6 mL of THF was treated with HCl (75 μL of a 4.3 M dioxane solution, 0.32 mmol, 10 equiv) with no appreciable color change. The solution was transferred to a screw-cap NMR tube fitted with a septum. The headspace was purged with 1 atm of O_2 for ca. 1 min, at which time the tube was shaken manually and then allowed to stand at room temperature. After 20 min the O_2 addition was repeated, and after 40 min $^{31}\text{P}\{^1\text{H}\}$ NMR indicates clean, quantitative conversion to **6**. The solution was transferred to a scintillation vial and concentrated under vacuum to yield a dark orange residue. The product was redissolved in a mixture of 2 mL of dichloromethane and 2 mL of hexane. The orange solution was concentrated in vacuo to liberate an orange powder, which was washed with 2 mL of hexane and dried in vacuo overnight. Yield: 45 mg (85%) of **6**·0.25(hexane). ^1H NMR and combustion analysis are both consistent with the presence of 0.25 equiv of hexane in the isolated product. ^1H NMR (500 MHz, CD_2Cl_2) δ/ppm : 5.05–5.16 (br, m, 4H), 4.86–5.00 (br, m, 8H), 4.49–5.59 (br, m, 4H), 3.03 (pseudoquintet, 6H), 2.13 (br, s, 6H), 2.03 (br, d, 12H), 1.66 (br, m, 12H). $^{31}\text{P}\{^1\text{H}\}$ NMR (121.5 MHz, CD_2Cl_2) δ/ppm : 112.6 (m, 4P). Elem. Anal.: Calcd. for $\text{C}_{40}\text{H}_{52}\text{Cl}_4\text{F}_{24}\text{N}_4\text{O}_8\text{P}_4\text{Rh}_2 \cdot 0.25(\text{C}_6\text{H}_{14})$: C, 29.92; H, 3.36; N, 3.36. Found: C, 30.01; H, 3.33; N, 3.34. Crystals suitable for X-ray diffraction were grown from THF/toluene solution as orange blocks.

X-Ray crystallographic details. Single crystals of **6** were obtained from a THF/toluene solution. Crystals were mounted on a Bruker three circle goniometer platform equipped with an APEX detector. A graphite monochromator was employed for wavelength selection of the Mo $\text{K}\alpha$ radiation ($\lambda = 0.71073 \text{ \AA}$). The data were processed and refined using the program SAINT supplied by Siemens Industrial Automation. Structures were solved by

Patterson methods or direct methods in SHELXS and refined by standard difference Fourier techniques in the SHELXTL program suite (6.10 v., Sheldrick G. M., and Siemens Industrial Automation, 2000). Hydrogen atoms bonded to carbon were placed in calculated positions using the standard riding model and refined isotropically; all non-hydrogen atoms were refined anisotropically. The structure $\text{Rh}_2(\text{tfepma})_2(\text{CNAd})_2\text{Cl}_4$, **6**, had one disordered trifluoroethoxy group that was satisfactorily modeled. Rotationally disordered CF_3 groups were modeled with the anisotropy of several of the minor fluorine positions constrained. Unit cell parameters, morphology, and solution statistics for the structure of **6** is summarized in Table S1.

Toepler pump measurements. Photolysis experiments were carried out in high-vacuum cells comprising a 1-cm fused quartz cuvette and a 20-mL solvent reservoir isolated from each other and the atmosphere by Teflon valves. HCl (from the reaction of NaCl with H_2SO_4) was transferred into the cell. Irradiation was carried out on samples maintained at 20 °C. After irradiation, the reaction solution was frozen, and noncondensable gas was passed through three U-traps maintained at 90 K and collected with a Toepler pump. The noncondensable gas was then combusted over hot CuO to confirm H_2 content.

Control experiments showed no production of H_2 , as determined by Toepler pump gas collection. Irradiation of a 50-mL solution of 0.1 M HCl in THF with light ($\lambda \geq 338$ nm) for 12 h gave only an insignificant quantity of noncondensable gas, which did not burn over CuO.⁴ Similarly, no H_2 was collected from solutions of **1** or **4** in THF containing excess HCl maintained at 20 °C in the dark for 12 h.

Data points in Figure 1 were all obtained as described above, except for the last two points, after 87 h and 130 h of photolysis. After the measurement at 66 h, more HCl was added to the sample, and the sample was then photolyzed for 21 h. The amount of H_2 produced at that point was added to the amount obtained after 66 h to obtain the 87 h data point. The 130 h data point was obtained similarly from the 87 h data point.

(4) A. F. Heyduk and D. G. Nocera, *Science* 2001, **293**, 1639.

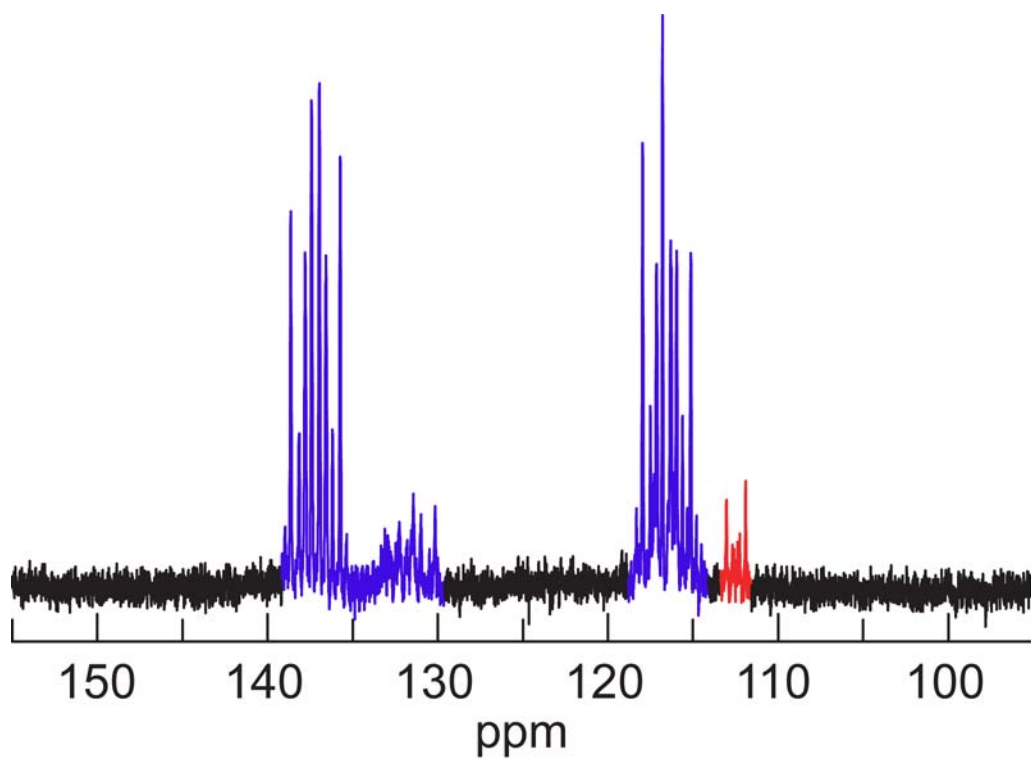


Figure S1. $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum for the products of photolyzing **2** in the presence of excess HCl in CD_2Cl_2 for ~3 h showing peaks assigned to **2** (blue) and **3** (red).

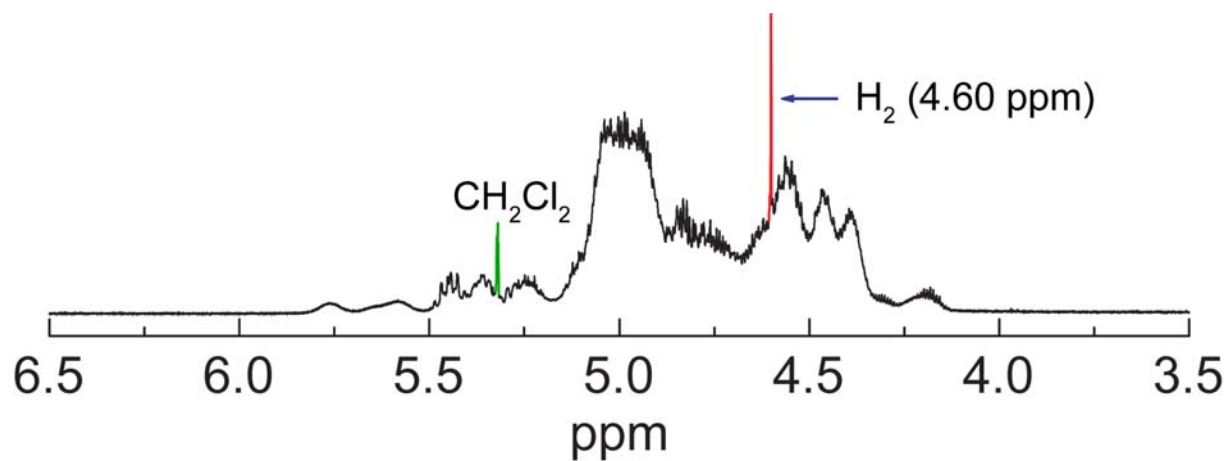


Figure S2. $-\text{OCH}_2\text{CF}_3$ region of the ^1H NMR spectrum for the products of photolyzing **2** in the presence of excess HCl in CD_2Cl_2 for ~ 12 h showing a peak at 4.60 ppm assigned to H_2 .

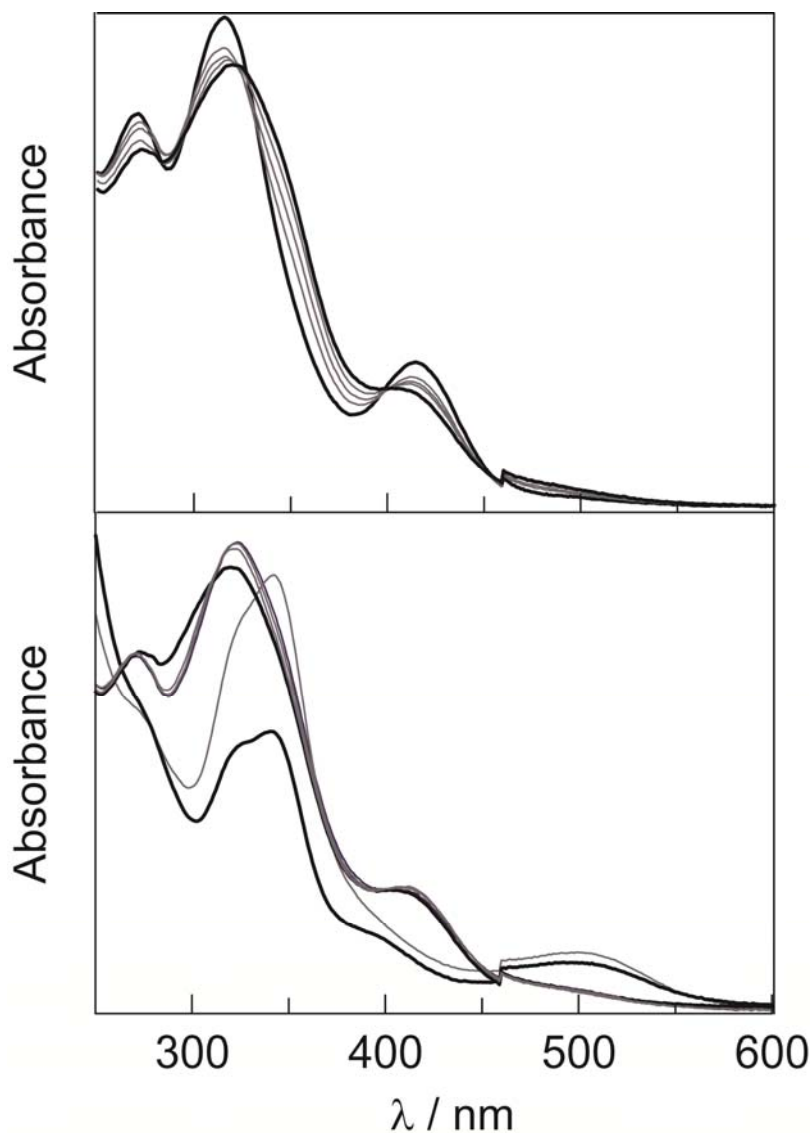


Figure S3. UV-vis traces of a photolysis experiment monitoring the progression of the absorption features of a solution of **1** with excess HCl under photolytic conditions. Data is divided in two regions: 0–4 min (0, 0.5, 1, 2, 4 min) (left) and 4–200 min (4, 6, 8, 10, 88, 200 min) (right). The photoreaction appears to involve three different regimes. At short times (0–4 min), the apparent buildup of a product is observed, with the isosbestic points at 323, 401 and 451 nm, reasonably close to the expected isosbestic points at 329, 392 and 446 nm. This intermediate is postulated to be tetrachloride **3** with some **2** also likely present. Between 6–10 min, a steady state is reached. In this regime, hydrogen production, HCl oxidative addition and Cl₂ elimination are balanced. After longer periods of time (88–200 min), **3** is clearly present, though the degradation of the complex is evident given the low absorbance between 300–400 nm, as well as an attendant increase in UV absorbance.

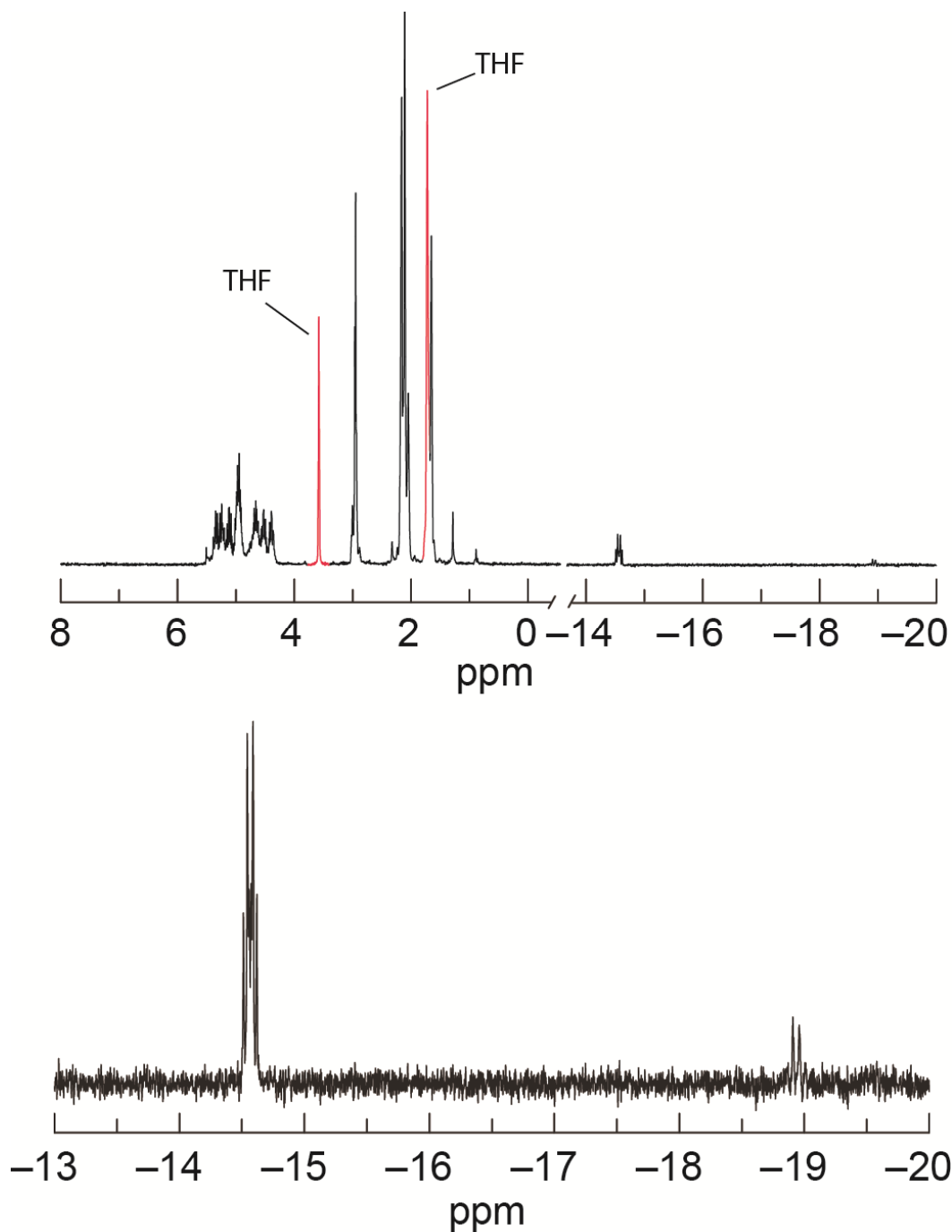


Figure S4. Full spectrum (top) and low-frequency region (bottom) of the ^1H NMR spectrum of a THF- d_8 solution of **5**. Low-frequency region showing Rh-H resonances attributed to the two isomers of **5**.

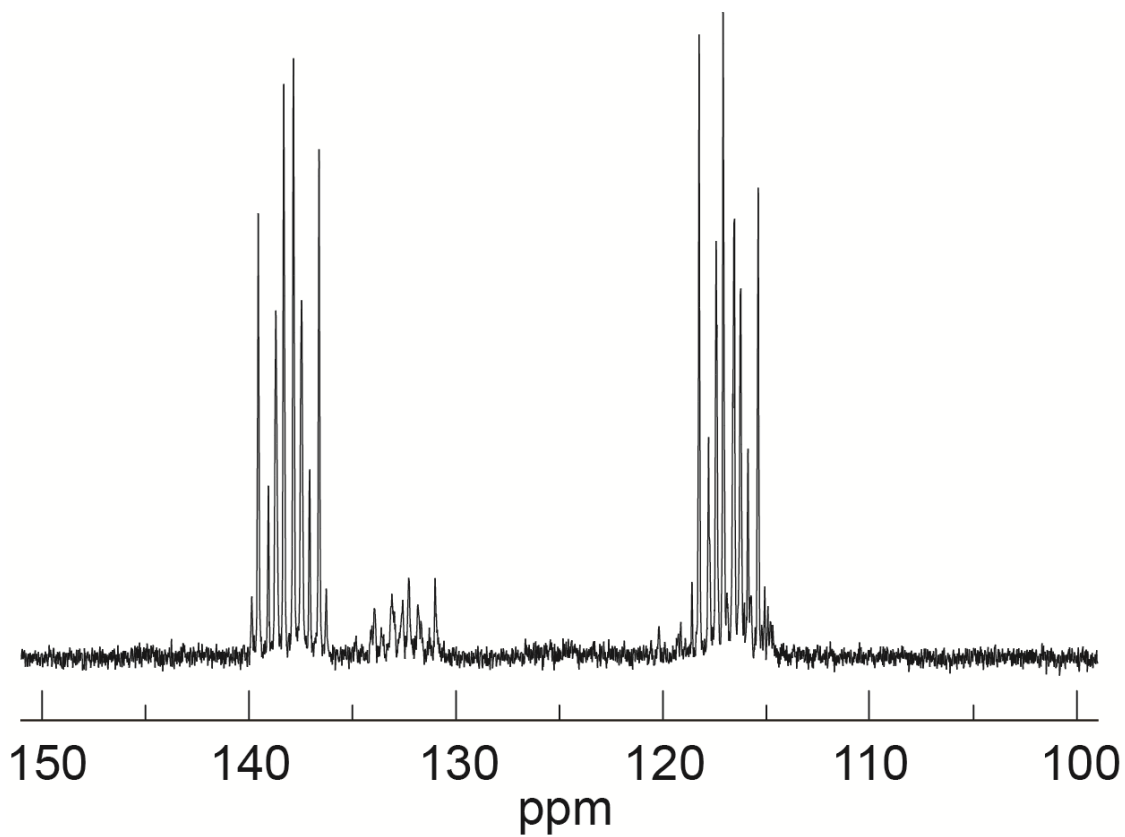


Figure S5. $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum of a THF- d_8 solution of **5**.

Table S1. Crystallographic data of **6**.

| | |
|---|--|
| Formula | C ₄₀ H ₅₂ Cl ₄ F ₂₄ N ₄ O ₈ P ₄ Rh ₂ |
| Fw, g/mol | 1644.36 |
| T(K) | 100(2) |
| Cryst. syst. | Triclinic |
| space group | <i>P</i> -1 |
| Color | Orange |
| <i>a</i> (Å) | 13.031(2) |
| <i>b</i> (Å) | 14.865(2) |
| <i>c</i> (Å) | 17.600(3) |
| α (°) | 80.155(3) |
| β (°) | 72.792(3) |
| γ (°) | 66.233(2) |
| <i>V</i> (Å ³) | 2975.3(9) |
| <i>Z</i> | 2 |
| no. refl. | 11322 |
| no. unique refl. | 9020 |
| <i>R</i> _{int} | 0.0470 |
| <i>R</i> ₁ ^b ; <i>wR</i> ₂ ^c (<i>I</i> > 2σ(<i>I</i>)) | 0.0468; 0.1140 |
| <i>R</i> ₁ ^b ; <i>wR</i> ₂ ^c (all data) | 0.0623; 0.1246 |
| <i>GOF</i> ^a on <i>F</i> ² | 1.024 |

^a *GOF* = $(\sum w(F_o^2 - F_c^2)^2 / (n - p))^{1/2}$ where *n* is the number of data and *p* is the number of parameters refined. ^b *R*₁ = $\sum ||F_o - |F_c|| / \sum |F_o|$. ^c *wR*₂ = $(\sum (w(F_o^2 - F_c^2)^2) / \sum (w(F_o^2)^2))^{1/2}$.