Electronic Supplementary Information (ESI) for:

Structural and chemical properties of half-sandwich rhodium complexes supported by the bis(2-pyridyl)methane ligand

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NMR Spectra



Figure S1. ¹H NMR (500 MHz, CD₃CN) of 1-Cl.



Figure S2. ¹³C{¹H} NMR (126 MHz, CD₃CN) of **1-Cl**.



Figure S3. Upper panel: ${}^{31}P{}^{1}H$ NMR (162 MHz, CD₃CN) of 1-Cl. Lower panel: ${}^{19}F$ NMR (376 MHz, CD₃CN) of 1-Cl.



Figure S5. HSQC spectrum (CD₃CN) of 1-Cl.



Figure S6. HMBC spectrum (CD₃CN) of 1-Cl.



Figure S7. NOESY spectrum (CD₃CN) of 1-Cl.



Figure S8. ¹H NMR (500 MHz, CD₃CN) of 1-NCCH₃.



Figure S9. ¹³C{¹H} NMR (126 MHz, CD₃CN) of 1-NCCH₃.



Figure S10. Upper panel: ${}^{31}P{}^{1}H$ NMR (162 MHz, CD₃CN) of 1-NCCH₃. Lower panel: ${}^{19}F$ NMR (376 MHz, CD₃CN) of 1-NCCH₃.

- 5.66



Figure S11. ¹H NMR of the product mixture from reduction of **1-NCCH**₃ with CoCp₂. The peak at δ 5.66 ppm corresponds to $[CoCp_2]^+$.¹



Figure S12. ¹H NMR (400 MHz) monitoring of reaction of **1-Cl** with Na(Hg) (10 equiv.). Lower panel: ¹H NMR of **1-Cl** (CD₃CN). Middle panels: ¹H NMR (C₆D₆) of reaction mixture after 30 min and 6 h reaction time. Inset: upfield region of spectrum of reaction mixture after 6 h indicating presence of metal–hydride species. Upper panel: ¹H NMR (C₆D₆) of dpma, confirming generation of free bidentate ligand upon reduction of **1-Cl** with Na(Hg).



Figure S13. ¹H NMR (400 MHz) of the product of the reaction of **1-NCCH**₃ with CoCp*₂ (1.9 equiv.). Lower panel: ¹H NMR of **1-NCCH**₃ (CD₃CN). Middle panel: ¹H NMR (C₆D₆) of reaction mixture following workup after 1 h reaction time. Insets: upfield and downfield regions of spectrum of reaction mixture after 1 h indicating presence of metal–hydride species and paramagnetic species, respectively. Upper panel: ¹H NMR (C₆D₆) of dpma, confirming generation of free bidentate ligand upon reduction of **1-NCCH**₃ with CoCp*₂.

Electronic Absorption Spectra



Figure S14. Electronic absorption spectrum (CH₃CN) of 1-Cl.



Figure S15. Electronic absorption spectrum (CH₃CN) of 1-NCCH₃.

Electrochemistry



Figure S16. CV data (CH₃CN, 0.1 M [ⁿBu₄N][PF₆]) for 1-Cl.



Figure S17. Comparison of CV data (CH₃CN, 0.1 M [${}^{n}Bu_{4}N$][PF₆]) for 1-Cl over the course of several cathodic scans. The 'Early' (blue line) and 'Late' (black line) data are separated by ca. 20 cathodic scans (over ~10 minutes).



Figure S18. Left panel: scan rate dependence data for **1-NCCH**₃. Right panel: plot of peak current density vs. (scan rate)^{1/2}, demonstrating the diffusional nature of the oxidized and reduced species involved in the redox couple in question. The relatively poor linearity of the observed peak current density (especially during cathodic scanning) with respect to (scan rate)^{1/2} is most likely due to the appearance of an additional cathodic process during repeated scans (marked with * in the CV data in the left panel), suggesting partial degradation of the complex upon reduction (see Main Text and Figure S21).



Figure S19. CV data (CH₃CN, 0.1 M [ⁿBu₄N][PF₆]) for 1-NCCH₃ at negative potentials.



Figure S20. Comparison of CV data for 1-NCCH₃ (scan rate = 2 V s⁻¹, blue line) and 2-NCCH₃ (scan rate = 0.1 V s^{-1} , black line).



Figure S21. Comparison of CV data (CH₃CN, 0.1 M [ⁿBu₄N][PF₆]) for **1-NCCH₃** over the course of several sequential cathodic scans. The new cathodic feature appearing just negative of $E_{pc}(Rh^{III/II})$ in later scans is marked with (*).

EPR Spectroscopy



Figure S22. Blue line: perpendicular-mode X-band EPR spectrum of the product of reduction of **1-NCCH**₃ with Cp₂Co (3:1 toluene/CH₃CN, 10 K, frequency = 9.64077 GHz, power = 2 mW). Black line: Easyspin simulation of EPR data; simulation parameters for component **A**: $g_x = 2.17$, $g_y = 2.03$, $g_z = 1.93$, $A_x = 7$ MHz, $A_y = 4$ MHz, $A_z = 25$ MHz, HStrain(x) = 151 MHz, HStrain(y) = 58 MHz, HStrain(z) = 113 MHz, linewidth = 1.85, weight = 1; component **B**: $g_{iso} = 2.04$, A = 34 MHz, HStrain = 96 MHz, linewidth = 17, weight = 0.87.

Crystallographic Information

Data Collection and Refinement Details

Crystals of **1-Cl** and **1-NCCH**₃ used for diffraction data collection were mounted on nylon loops using Paratone oil under a nitrogen stream. Low temperature (200 K) data were obtained with X-rays from a Bruker generator using a fine focus Mo sealed tube running at 30mA and 50kV (**1-Cl**, Mo K_{α} = 0.71073 Å; SMART APEX detector positioned at 50.0 mm and equipped with a MonoCap collimator and graphite monochromator) or a Bruker MicroStar microfocus rotating anode generator running at 60 mA and 45 kV (**1-NCCH**₃, Cu K_{α} = 1.54178 Å; APEX II detector positioned at 50.0 mm and equipped with Helios multilayer mirror optics). All diffractometer manipulations, including data collection, integration and scaling were carried out using the Bruker APEXII software.² Absorption corrections were applied using SADABS.³ Space groups were determined on the basis of systematic absences and intensity statistics and the structures were solved by intrinsic phasing using XT⁴ or by direct methods using XS⁵ (incorporated into SHELXTL) and refined by full-matrix least squares on F². All non-hydrogen atoms were refined using anisotropic displacement parameters. All hydrogen atoms were placed in idealized positions and refined using a riding model. The structures were refined (weighted least squares refinement on F²) to convergence using the Olex software package equipped with XL.^{5,6}

	1-Cl	1-NCCH ₃
CCDC number	1912972	1912971
empirical formula	$C_{10.5}H_{12.5}Cl_{0.5}F_3NP_{0.5}Rh_{0.5}$	$C_{92}H_{112}F_{48}N_{12}P_8Rh_4$
formula wt	294.38	2957.33
Т (К)	200	200
a, Å	13.882(2)	16.7908(7)
b, Å	12.3599(19)	15.7747(6)
c, Å	13.397(2)	10.9869(5)
α, deg	90	90
β, deg	90	90
γ, deg	90	90
$V, Å^3$	2298.6(6)	2910.1(2)
Z	8	1
crystal dimensions (mm.)	0.56 imes 0.37 imes 0.27	$0.12\times0.06\times0.04$
cryst syst	orthorhombic	orthorhombic
space group	Pnma	Pnma
$\rho_{calcd}, g/cm^3$	1.701	1.687
2θ range, deg	4.226 to 66.332	9.62 to 141.02
wavelength (Å)	0.71073	1.54178
reflections collected	30764	26516
indep. reflections/R _{int}	4506/0.0348	2850/0.0908
μ , mm ⁻¹	0.989	6.686
abs corr	Multi-scan	Multi-scan
GOOF^{c}	1.039	1.033
Data/restraints/parameters	4506/0/166	2850/0/212
$\mathbf{R}_{1},^{a}\mathbf{w}\mathbf{R}_{2}^{b}(\mathbf{I} \geq 2\sigma(\mathbf{I}))$	0.0371, 0.0916	0.035, 0.0831
R_1 , ^{<i>a</i>} w R_2 ^{<i>b</i>} (all data)	0.0488, 0.1012	0.0408, 0.0867

Table S1. Crystal and Refinement Data

 ${}^{a} R_{1} = \frac{\sum ||F_{o}| - |F_{c}|| / \sum |F_{o}| - b wR_{2}}{\sum ||F_{o}| - |F_{c}|| / \sum |F_{o}| - b wR_{2}} = \left[\sum ||w(F_{o}^{2} - F_{c}^{2})^{2}|| / \sum |w(F_{o}^{2} - F_{c}^{2})^{2}|| / \sum ||w(F_{o}^{2} - F_{c}^{2})^{2}|| / \sum ||F_{o}| - |F_{c}|| / \sum ||F_{o}|| / \sum |$

Special Refinement Details for 1-Cl

No special refinement necessary.



Figure S23. Solid-state structure (XRD) of **1-Cl**. Hydrogen atoms except for H6A and H6B omitted for clarity. Thermal displacement ellipsoids shown at 50% probability level.

Special Refinement Details for 1-NCCH3

One of the two outer-sphere PF_6^- counteranions in **1-NCCH**₃ was disordered over two positions, in addition to being located on a crystallographic symmetry element. This disorder was satisfactorily modelled as two PF_6^- orientations with fixed 50:50 occupancy.



Figure S24. Solid-state structure (XRD) of **1-NCCH**₃. Hydrogen atoms except for H6A and H6B omitted for clarity. Both orientations (50:50 occupancy) of disordered PF_6^- counteranions shown. Thermal displacement ellipsoids shown at 50% probability level.

References

- (1) S. Vanicek, H. Kopacka, K. Wurst, T. Müller, H. Schottenberger and B. Bildstein, *Organometallics*, 2014, **33**, 1152-1156.
- (2) APEX2, Version 2 User Manual, M86-E01078,, Bruker Analytical X-ray Systems, Madison, WI, 2006.
- (3) G. M. Sheldrick, SADABS (version 2008/1): Program for Absorption Correction for Data from Area Detector Frames, 2008, University of Göttingen
- (4) G. Sheldrick, Acta Crystallogr., Sect. A: Found. Crystallogr., 2015, 71, 3-8.
- (5) G. Sheldrick, Acta Crystallogr., Sect. C: Cryst. Struct. Commun., 2015, 71, 3-8.
- (6) O. V. Dolomanov, L. J. Bourhis, R. J. Gildea, J. A. K. Howard and H. Puschmann, *J. Appl. Crystallogr.*, 2009, **42**, 339-341.