Supporting Information

Half-Rotation in a Kinetically Locked [2]Catenane Induced By Transition Metal Ion Substitution

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1. General Experimental Section

Unless stated otherwise, all reagents and solvents were purchased from Aldrich Chemicals and used without further purification. Column chromatography was carried out using Silica 60A (particle size 35-70 µm, Fisher, UK) as the stationary phase, and TLC was performed on precoated silica gel plates (0.25 mm thick, 60 F254, Merck, Germany) and observed under UV light. NMR spectra were recorded on Bruker AV 400, and Bruker DMX 500 instruments. Chemical shifts are reported in parts per million (ppm) from low to high frequency and referenced to the residual solvent resonance. Coupling constants (*J*) are reported in hertz (Hz). Standard abbreviations indicating multiplicity were used as follows: s = singlet, d = doublet, t = triplet, dd = double doublet, q = quartet, m = multiplet, b = broad, ddd = doublet of double doublets. ^1H and ^{13}C NMR assignments were made using 2D-NMR methods (COSY, ROESY, TOCSY, HSQC, HMBC) and are unambiguous unless stated otherwise. Melting points (m.p.) were determined using a Sanyo Gallenkamp apparatus and are reported uncorrected. Low resolution ESI mass spectrometry was performed with a Finnigan LCQ-MS, Micromass Platform II or Waters Quattro Ultima LC-*MS*/*MS* mass spectrometers. High resolution ESI and FAB mass spectrometry were carried out by the mass spectrometry services at the University of Edinburgh and the EPSRC National Mass Spectrometry Service Centre, Swansea, UK. Compounds **1**H_2[1] and **2**$Pd(CH_3CN)$[2] were prepared as reported previously.

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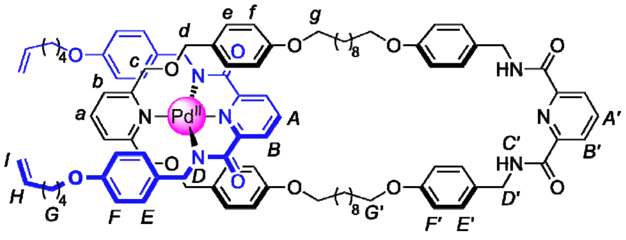
[1] A.-M. L. Fuller, D. A. Leigh, P. J. Lusby, A. M. Z. Slawin and D. B. Walker, *J. Am. Chem. Soc*, 2005, **127**, 12612.

[2] A.-M. Fuller, D. A. Leigh, P. J. Lusby, I. D. H. Oswald, S. Parsons and D. B. Walker, *Angew. Chem., Int. Ed*, 2004, **43**, 3914.

2. Synthetic Procedures and NMR Spectra



2Pd(**1**H$_2$): A solution of **1**H$_2$ (0.288 g, 0.287 mmol) and **2**Pd(CH$_3$CN) (0.197 g, 0.287 mmol) in anhydrous CH$_2$Cl$_2$ (20 mL) was stirred for 1 h at room temperature. The solution was concentrated under reduced pressure and the crude residue purified by column chromatography, (98:2 CH$_2$Cl$_2$:MeOH) to yield **2**Pd(**1**H$_2$): as a yellow, solid (0.45 g, yield = 95%). m.p. 98-99 °C; ^{1}H NMR (500 MHz, CD$_2$Cl$_2$, 298 K): δ = 1.15-1.51 (m, 32H, alkyl-H), 1.71 (m, 8H, alkyl-H), 2.07 (m, 4H alkyl-H), 3.82 (m, 8H, H$_{G'}$ + H$_G$), 3.92 (t, 4H, J = 6.6 Hz, H$_g$), 4.32 (s, 4H, H$_d$), 4.45 (s, 4H, H$_c$), 4.49 (d, 4H, J = 6.1 Hz, H$_{D'}$), 4.54 (s, 4H, H$_d$), 4.98 (m, 4H, H$_H$), 5.81 (m, 2H, H$_I$), 6.41 (d, 4H, J = 8.6 Hz, H$_F$), 6.55 (d, 4H, J = 8.6 Hz, H$_E$), 6.70 (d, 4H, J = 8.6 Hz, H$_{F'}$), 6.79 (d, 4H, J = 8.6 Hz, H$_f$), 7.18 (m, 8H, H$_e$ + H$_{E'}$), 7.45 (d, 2H, J = 7.8 Hz, H$_b$), 7.66 (d, 2H, J = 7.8 Hz, H$_B$), 7.88 (t, 1H, J = 7.8 Hz, H$_a$), 7.95 (t, 1H, J = 7.8 Hz, H$_A$), 8.02 (t, 1H, J = 7.8 Hz, H$_{A'}$), 8.32 (d, J = 7.8 Hz, 2H, H$_{B'}$), 8.72 (t, J = 6.3 Hz, 2H, H$_{C'}$); (^{13}C NMR (125 MHz, CD$_2$Cl$_2$, 298 K) δ =25.89, 26.13, 26.38, 29.24, 29.33 (x2), 29.34, 29.58, 29.61, 29.63, 29.75, 34.04, 43.18, 49.14, 68.34, 68.44, 72.08, 73.7, 114.61, 114.75, 114.95, 114.97, 122.68, 124.86, 125.32, 128.94, 129.37, 129.79, 130.07, 131.18, 133.57, 139.22, 139.34, 139.96, 141.02, 149.75, 153.03, 158.52, 158.87, 159.52, 160.89, 164.14, 171.59; ESI-MS: m/z = 1651 [MH]$^+$; HRESI-MS: m/z = 1650.7558 (calcd. for C$_{95}$H$_{114}$N$_7$O$_{12}$Pd, 1650.7583).

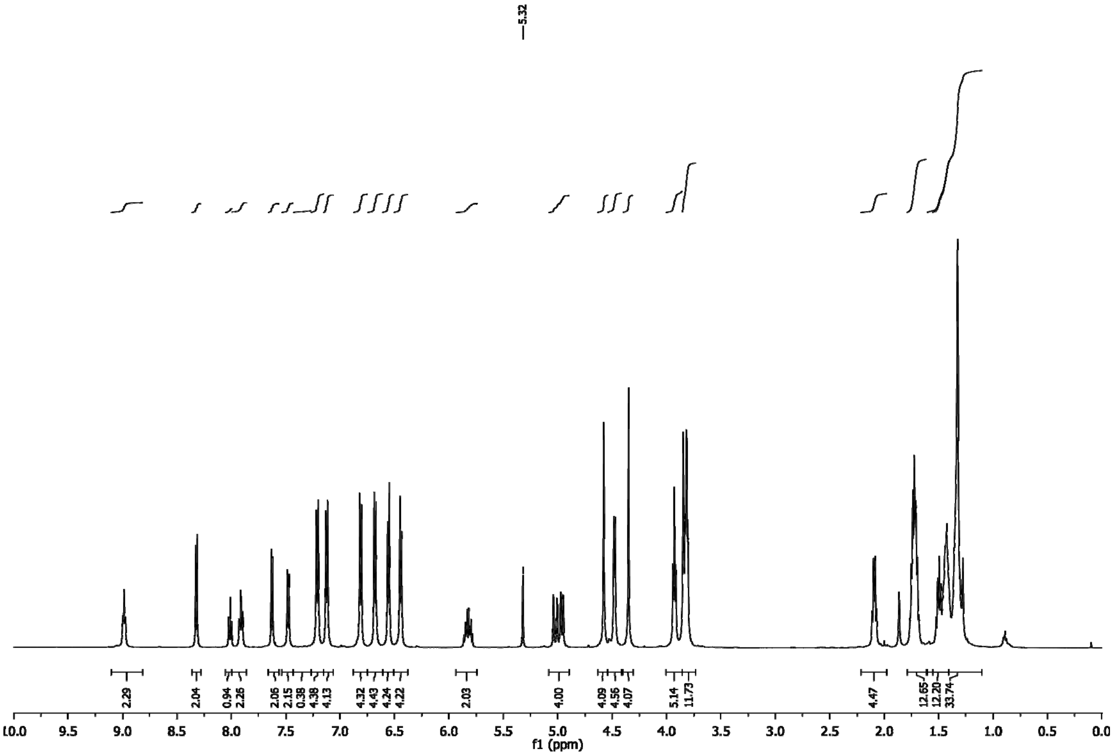


Figure S1. ^1H NMR spectrum of 2Pd(1H$_2$).

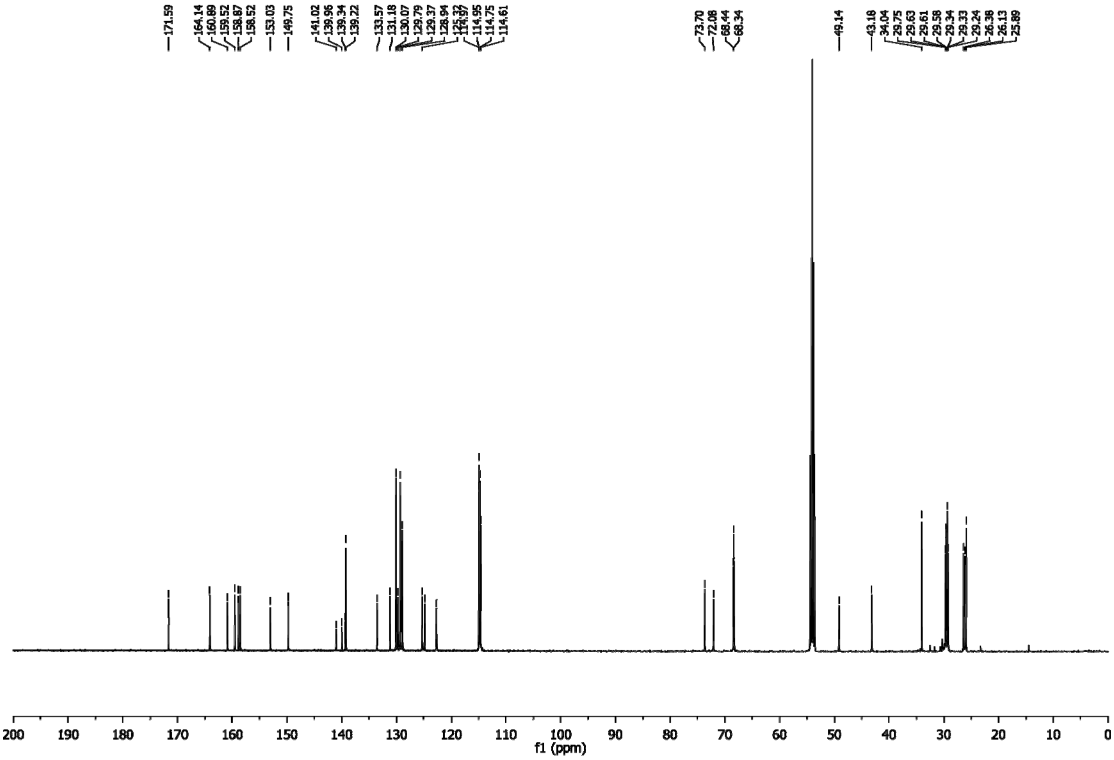
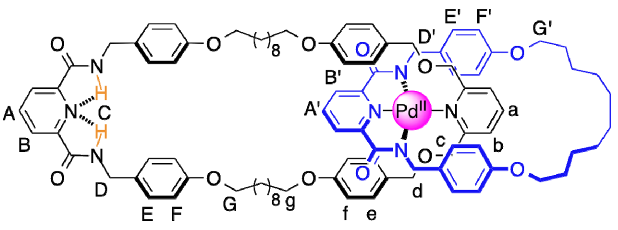


Figure S2. ^{13}C NMR spectrum of 2Pd(1H$_2$).



Pd**3**H_2: (a) A solution of **2**Pd(**1**H_2) (0.44 g, 0.26 mmol) in anhydrous dichloromethane (100 mL) was added via a double ended needle to a solution of first generation Grubbs’ catalyst (0.064 g, 0.077 mmol) in anhydrous dichloromethane (500 mL) under an atmosphere of nitrogen. The solution was stirred at room temperature for 18 h, concentrated under reduced pressure and the crude residue purified by column chromatography (98:2 CH_2Cl_2:MeOH) to yield a yellow solid (0.28 g).

(b) To a stirred solution of the yellow solid obtained in part (a) (0.28 g) in THF (50 mL), was added 10% w/w Pd-C (0.04 g) and the resultant suspension stirred under an atmosphere of hydrogen for 18 h. The suspension was filtered through a plug of Celite, and the solution concentrated under reduced pressure to yield Pd**3**H_2 as a yellow solid (0.272 g, yield = 64% over two steps). m.p. 158-159 °C; ^{1}H NMR (400 MHz, CD_2Cl_2, 298 K): δ= 1.25-1.38 (m, 24H, alkyl-H), 1.41 (m, 12H, alkyl-H), 1.72 (m, 12H, alkyl-H), 3.82 (t, 4H, J = 6.5 Hz, H_g), 3.87 (m, 8H, $H_G + H_{G'}$), 3.96 (s, 4H, $H_{D'}$), 4.45 (s, 4H, H_d), 4.52, (d, J = 6.1 Hz, 4H, H_D), 4.64 (s, 4H, H_c), 6.23 (d, 4H, J = 8.6 Hz, $H_{F'}$), 6.33 (d, 4H, J = 8.6 Hz, $H_{E'}$), 6.68 (d, 4H, J = 8.4 Hz, H_F), 6.76 (d, 4H, J = 8.6 Hz, H_f), 7.14 (d, 4H, J = 8.4 Hz, H_E), 7.22 (m, 6H, H_e+H_b), 7.58 (d, 2H, J = 7.8 Hz, $H_{B'}$), 7.74 (t, 1H, J = 7.8 Hz, $H_{A'}$), 7.87 (t, 1H, J = 7.8 Hz, H_a), 8.04 (t, 1H, J = 7.8 Hz, H_A), 8.34 (d, 2H, J = 7.8 Hz, H_B), 8.88 (t, 2H, J = 6.1 Hz, H_C); ^{13}C NMR (125 MHz, CD_2Cl_2, 298 K): δ= 25.99, 26.01, 26.23, 29.00, 29.01, 29.05, 29.26 (x2), 29.32, 29.34, 29.68, 30.07, 43.23, 50.02, 67.64, 68.36, 68.39, 71.99, 73.76, 114.82, 114.9, 114.95, 122.3, 124.83, 125.33, 128.61, 129.34, 129.48 (x2), 130.61, 131.08, 133.14, 139.39, 140.84, 149.77, 152.95, 158.04, 158.91, 159.64, 160.47, 164.06, 171.71; LRFAB-MS (3-NOBA matrix): m/z = 1624 $[M]^+$; HRFAB-MS (3-NOBA matrix): m/z = 1624.73425 (calcd. for $^{12}C_{92}{}^{13}C_1H_{111}N_7O_{12}Pd$, 1624.73563).

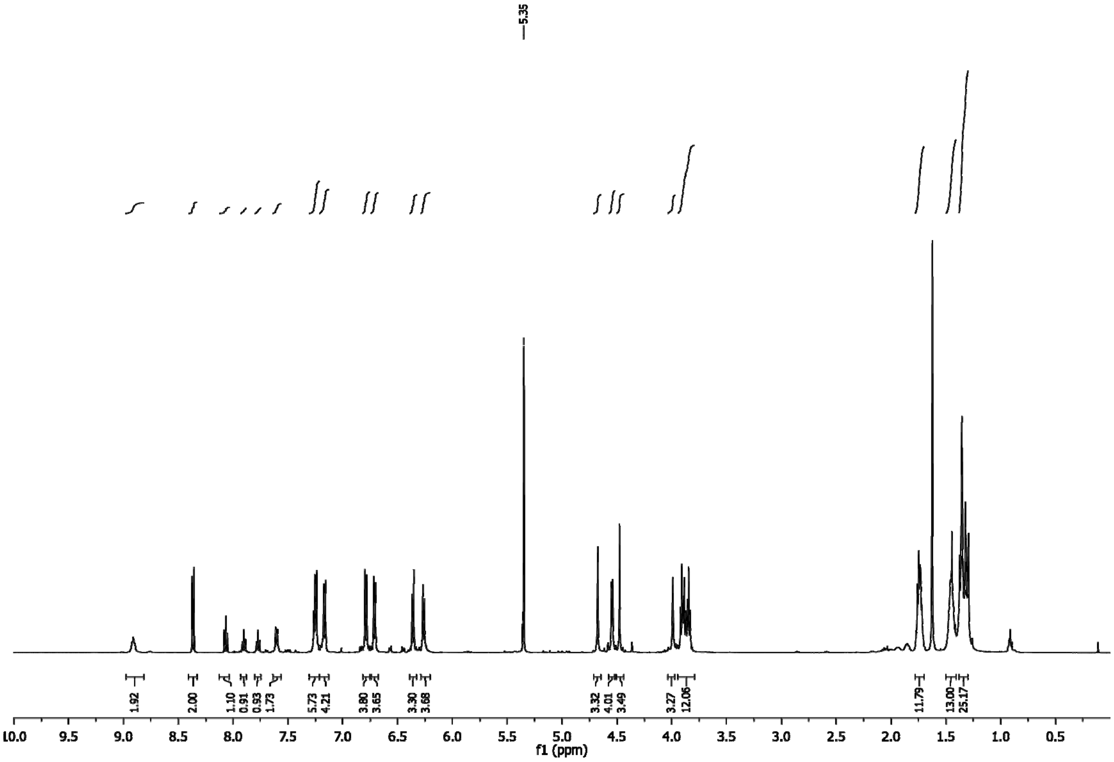


Figure S3. ^{1}H NMR spectrum of Pd**3**H$_2$.

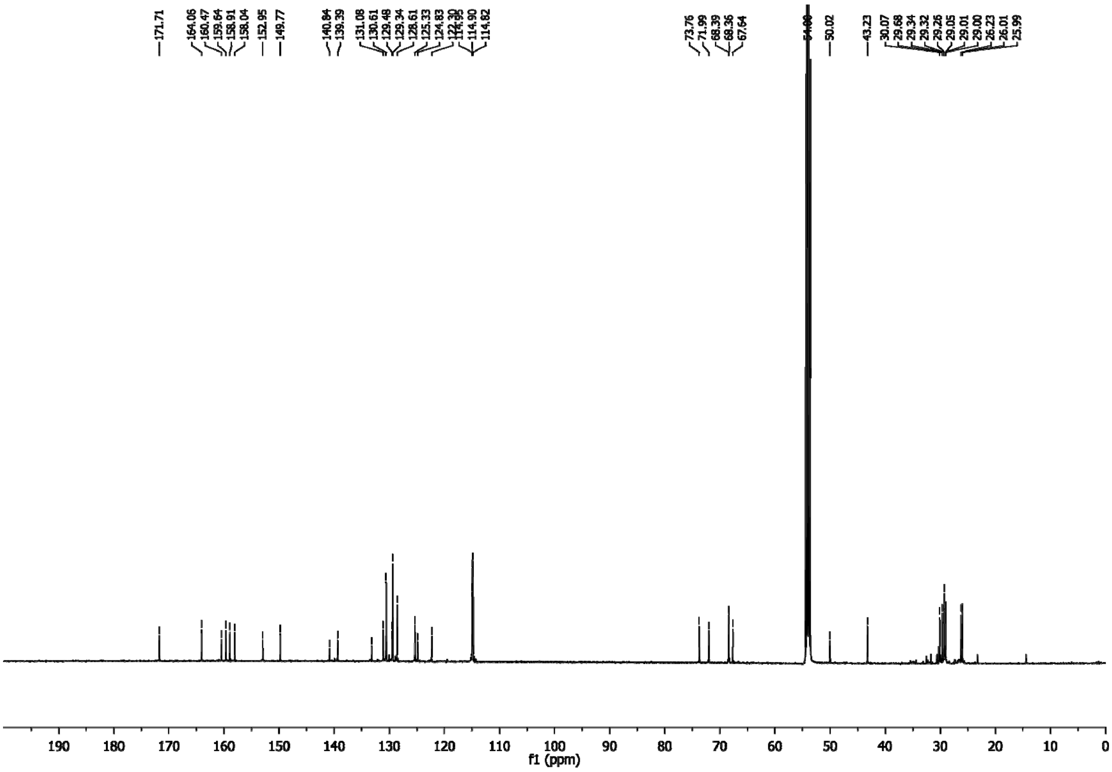
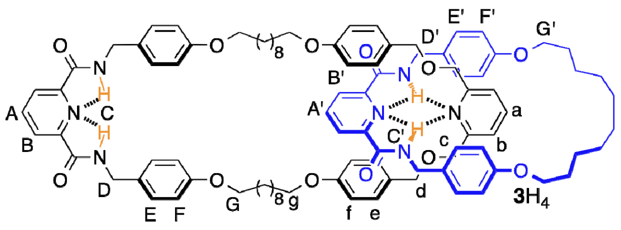


Figure S4. ^{13}C NMR spectrum of Pd**3**H$_2$.



$3H_4$: To a solution of Pd**3**H_2 (0.215 g, 0.132 mmol) in dichloromethane (20 mL) and methanol (20 mL) was added potassium cyanide (0.086 g, 1.32 mmol) in methanol (5 mL). The solution was stirred at room temperature for 1 h, until it was colourless, and then heated gently to reduce the overall volume to less than 5 mL. The resultant mixture was dispersed in water (25 mL) and washed with dichloromethane (3 x 25 mL). The combined organic extracts were washed with further water (25 mL) and dried over anhydrous magnesium sulfate. After filtration, the solution was concentrated under reduced pressure and the crude residue recrystallised from acetonitrile to give **3**H_4 as a colourless solid (0.198 g, yield = 98%). m.p. 139-141 °C; ^1H NMR (400 MHz, CD_2Cl_2, 298 K): δ = 1.26-1.41 (m, 24H, alkyl-H), 1.41 (m, 12H, alkyl-H), 1.69 (m, 12H, alkyl-H), 3.81 (m, 12H, $H_G + H_g + H_{g'}$), 4.13 (s, 4H, H_d), 4.18 (d, 4H, J = 6.2 Hz, $H_{D'}$), 4.30 (s, 4H, H_c), 4.50 (d, 4H, J = 6.1 Hz, H_D), 6.41 (d, 4H, J = 8.8 Hz, $H_{F'}$), 6.74 (m, 8H, $H_{E'} + H_f$), 6.74 (d, 4H, J = 8.8 Hz, H_F), 7.00 (d, 4H, J = 8.6 Hz, H_e), 7.06 (d, 2H, J = 7.7 Hz, H_b), 7.13 (d, 4H, J = 8.8 Hz, H_E), 7.53 (t, 1H, J = 7.7 Hz, H_a), 7.97 (t, 1H, J = 7.6 Hz, $H_{A'}$), 8.05 (m, 3H, H_A+H_C), 8.28 (d, 2H, J = 7.6 Hz, $H_{B'}$), 8.34 (d, 2H, J = 7.7 Hz, H_B), 8.94 (t, 2H, J = 6.2 Hz, $H_{C'}$); ^{13}C NMR (125 MHz, CD_2Cl_2, 298 K): δ = 26.05, 26.46 (x2), 28.87, 29.05, 29.66, 29.72, 29.78, 29.84, 29.93, 29.95 (x2), 42.89, 43.33, 67.54, 68.34, 68.51, 71.97, 73.1, 114.41, 114.64, 114.92, 120.23, 125.18, 125.54, 129.42 (x2), 129.92, 130.21, 130.55, 130.77, 137.4, 138.71, 139.48, 149.6, 149.64, 158.16, 158.25, 158.97, 159.13, 163.73, 163.80; LRFAB-MS (3-NOBA matrix): m/z = 1522 $[M+1]^+$; HRFAB-MS (3-NOBA matrix): m/z = 1521.85493 (calcd. for $C_{92}{}^{13}C_1H_{114}N_7O_{12}$, 1521.85590).

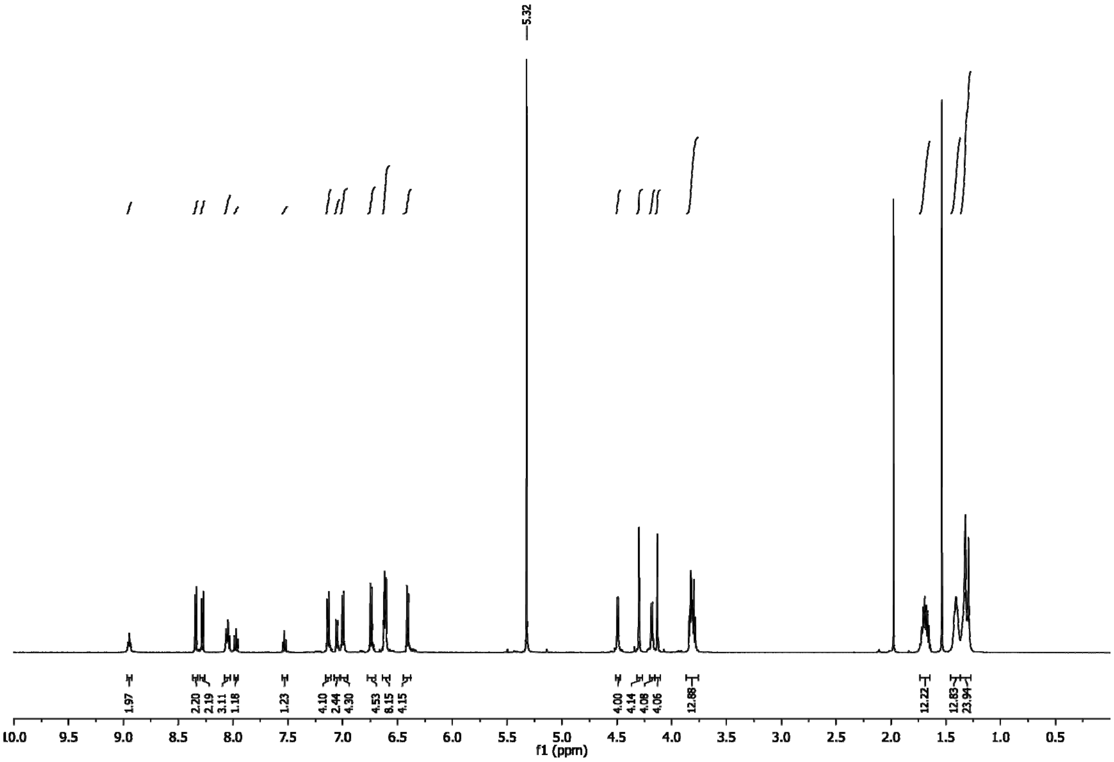


Figure S5. ^{1}H NMR spectrum of **3**H_4.

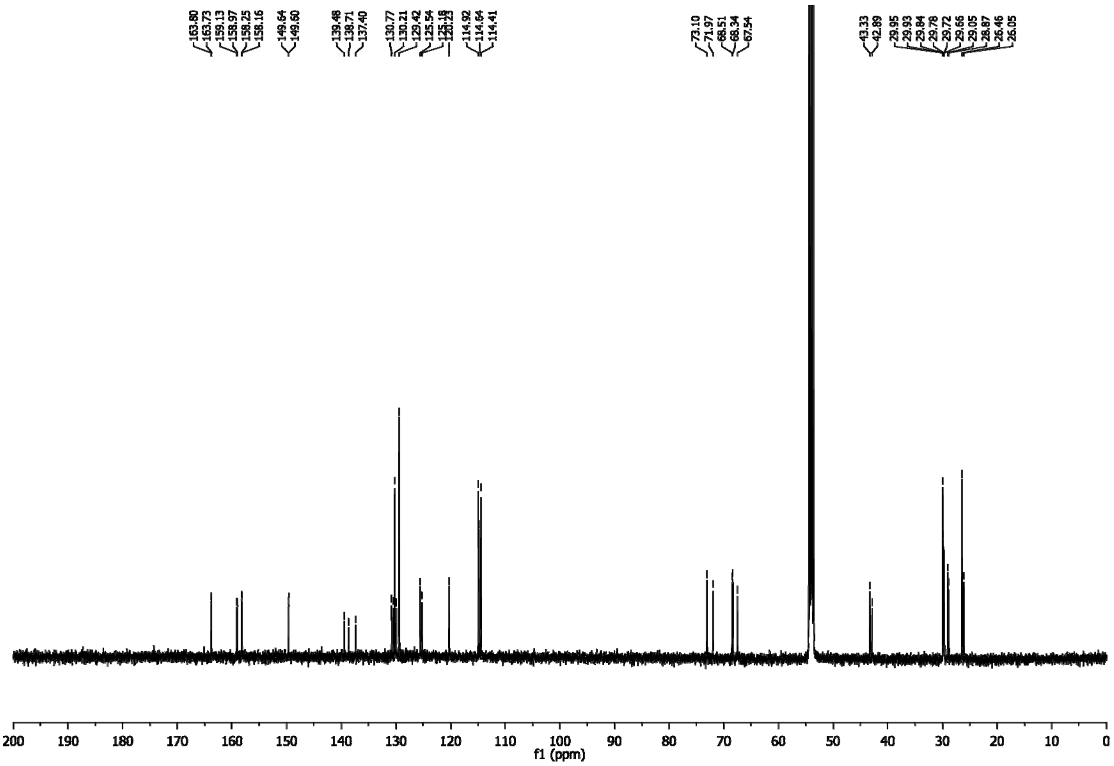
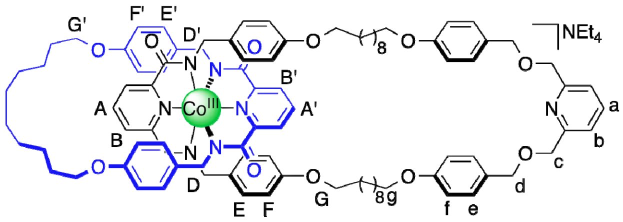


Figure S6. ^{13}C NMR spectrum of **3**H_4.



[Co**3**]NEt_4: To a solution of **3**H_4 (0.100 g, 0.066 mmol) in ethanol (15 mL) was added $Co(OAc)_2.(H_2O)_4$ (0.016 g, 0.066 mmol) and $Et_4NOAc.(H_2O)_4$ (0.017 g, 0.066 mmol) and stirred with gentle heating (35 °C) for 15 minutes. Sodium hydride (0.011 g, 0.26 mmol) was then mixed with ethanol (1 mL) and the resultant sodium ethoxide solution added drop-wise to the reaction mixture. The solution was left to stir for 3 h at room temperature whilst being exposed to a gentle flow of air. The resultant green suspension was filtered, the solvent removed under reduced pressure and the crude residue purified by column chromatography (60:39:1 CH_2Cl_2:CH_3COCH_3:Et_3N) to yield the title compound as a dark green solid (0.084 g, yield = 81%). m.p. 91-92 °C; ^{1}H NMR (400 MHz, CD_2Cl_2, 298 K): $\delta = 1.19$ (t, 12H, $J = 7.3$ Hz, $N(CH_2\underline{CH_3})_4$, 1.33-1.50 (m, 36H, alkyl-H), 1.66-1.87 (m, 12H, alkyl-H), 3.12 (q, 8H, $J = 7.3$ Hz, $N(\underline{CH_2}CH_3)_4$), 3.28 (s, 4H, $H_{D'}$), 3.37 (s, 4H, H_D), 3.84 (t, 4H, $J = 6.6$ Hz, $H_{G'}$), 3.94 (m, 8H, $H_g + H_G$), 4.54, (s, 4H, H_c), 4.55 (s, 4H, H_d), 6.15 (d, 4H, $J = 8.6$ Hz, $H_{F'}$), 6.36 (d, 4H, $J = 8.6$ Hz, $H_{E'}$), 6.42 (d, 4H, $J = 8.8$ Hz, H_F), 6.48 (d, 4H, $J = 8.8$ Hz, H_E), 6.86 (d, 4H, $J = 8.8$ Hz, H_f), 7.27 (d, 4H, $J = 8.8$ Hz, H_e), 7.35 (m, 4H, $H_b + H_B$), 7.70 (t, 1H, $J = 7.6$ Hz, H_a), 7.75 (d, 2H, $J = 7.8$ Hz, $H_{B'}$), 7.79 (t, 1H, $J = 7.6$ Hz, H_A), 8.09 (t, 1H, $J = 7.8$ Hz, $H_{A'}$); ^{13}C NMR (100 MHz, CD_2Cl_2, 298 K): $\delta = 7.91$, 26.05, 26.42, 26.53, 28.77, 28.86, 29.64, 29.72 (x2), 29.77 (x2), 29.93 (x2), 46.36, 46.63, 53.03, 68.03, 68.50, 68.56, 72.89, 73.16, 113.84, 114.76, 114.82, 120.7, 122.23, 123.00, 128.07, 129.2, 130.09 (x2), 130.54, 133.41, 134.41, 137.55, 138.84, 157.15, 157.61, 158.01, 158.52, 158.6, 159.40, 168.98, 169.16; ESI-MS: $m/z = 1578$ $[MH]^+$; HRESI-MS: $m/z = 1577.73609$ (calcd. for $C_{93}H_{110}CoN_7O_{12}$, 1577.76496).

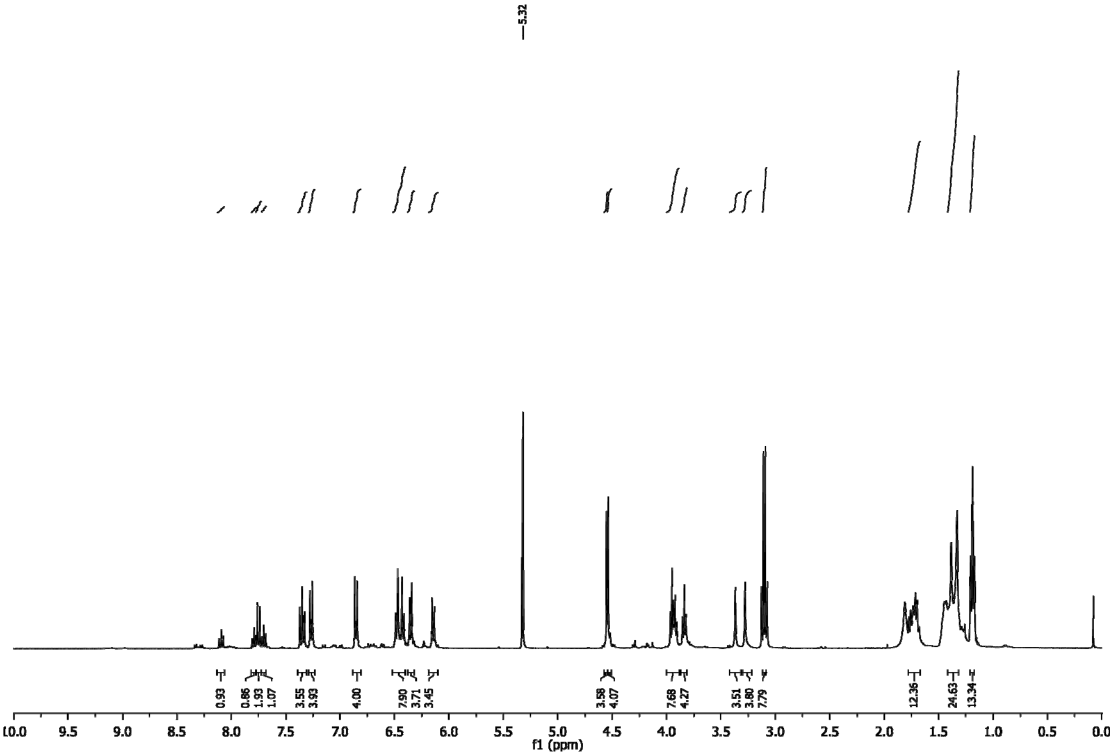


Figure S7. ^{1}H NMR spectrum of [Co**3**]NEt_4.

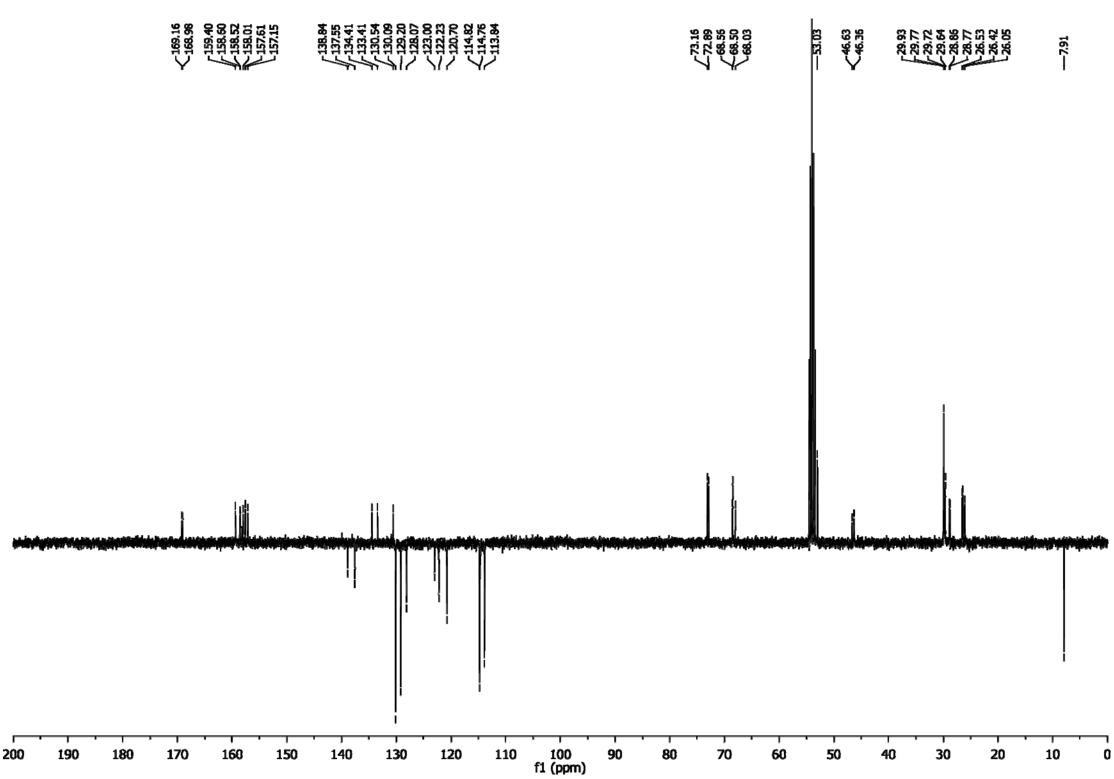


Figure S8. ^{13}C NMR spectrum of [Co**3**]NEt_4.

Conversion of [Co**3**]NEt_4 to **3**H_4:

[Co**3**]NEt_4 (20 mg, 11.7 µmol) was dissolved in MeOH (5 ml) and AcOH (5 ml) and activated Zn (0.050 g) was added and the resulting suspension was stirred for 30 min. under an atmosphere of air. The solvent was removed under reduced pressure and the crude residue was redissolved in $CHCl_3$ (25 mL) and washed with a 17.5% NH_3 solution saturated with Na_4EDTA (50 mL). The aqueous layer was extracted with $CHCl_3$ (3 x 25 mL). The combined organic layers were washed with brine (50 mL), dried (Na_2SO_4) and purified by column chromatography on silica gel (98:2 CH_2Cl_2:MeOH as eluent) to yield **3**H_4 as a colorless solid (16 mg, 90%).

Conversion of **3**H_4 to Pd**3**H_2:

To a solution of **3**H_4 (15 mg, 9.86 µmol) dissolved in CH_2Cl_2 (3 mL) and CH_3CN (1mL) was added $Pd(OAc)_2$, (2.5 mg, 10.8 µmol, 1.1 eq.) and the solution was stirred for 8 h and the solvent was removed under reduced pressure. The crude residue was purified by column chromatography on silica gel (98:2 CH_2Cl_2:MeOH as eluent) to yield Pd**3**H_2 as a pale yellow solid (11 mg, 71%).

3. X-ray Crystallographic Data

Pd**3**H$_2$

Identification code	Pd3H2	
Empirical formula	C97 H117 N9 O12 Pd	
Formula weight	1707.40	
Temperature	93(2) K	
Wavelength	0.71073 Å	
Crystal system	Triclinic	
Space group	P-1	
Unit cell dimensions	a = 13.579(2) Å	α= 77.683(8)°.
	b = 17.669(3) Å	β= 74.610(8)°.
	c = 19.456(3) Å	γ = 81.063(8)°.
Volume	4373.2(13) Å^3	
Z	2	
Density (calculated)	1.297 Mg/m^3	
Absorption coefficient	0.280 mm^{-1}	
F(000)	1808	
Crystal size	0.10 x 0.03 x 0.01 mm^3	
Theta range for data collection	2.06 to 25.39°.	
Index ranges	-16<=h<=16, -19<=k<=21, -23<=l<=23	
Reflections collected	44474	
Independent reflections	15933 [R(int) = 0.0905]	
Completeness to theta = 25.00°	99.5 %	
Absorption correction	Multiscan	
Max. and min. transmission	1.000 and 0.693	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	15933 / 9 / 1081	
Goodness-of-fit on F^2	0.956	
Final R indices [I>2sigma(I)]	R1 = 0.1191, wR2 = 0.2963	
R indices (all data)	R1 = 0.1641, wR2 = 0.3327	
Largest diff. peak and hole	0.776 and -0.607 e.Å^{-3}	
CCDC number	874997	

3H_4

Identification code	3H4	
Empirical formula	C93 H113 N7 O12	
Formula weight	1520.90	
Temperature	173(2) K	
Wavelength	1.54178 Å	
Crystal system	Monoclinic	
Space group	P2(1)/c	
Unit cell dimensions	a = 28.663(11) Å	α= 90°.
	b = 11.665(4) Å	β= 115.997(9)°.
	c = 28.056(11) Å	γ = 90°.
Volume	8432(5) $Å^3$	
Z	4	
Density (calculated)	1.198 Mg/m^3	
Absorption coefficient	0.631 mm^{-1}	
F(000)	3264	
Crystal size	0.12 x 0.05 x 0.05 mm^3	
Theta range for data collection	1.71 to 67.20°.	
Index ranges	-34<=h<=33, -13<=k<=13, -33<=l<=33	
Reflections collected	112492	
Independent reflections	14994 [R(int) = 0.1994]	
Completeness to theta = 67.00°	99.6 %	
Absorption correction	Multiscan	
Max. and min. transmission	1.000 and 0.8464	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	14994 / 40 / 1026	
Goodness-of-fit on F^2	1.288	
Final R indices [I>2sigma(I)]	R1 = 0.1259, wR2 = 0.3598	
R indices (all data)	R1 = 0.1798, wR2 = 0.4100	
Largest diff. peak and hole	0.939 and -0.482 e.$Å^{-3}$	
CCDC number	874998	

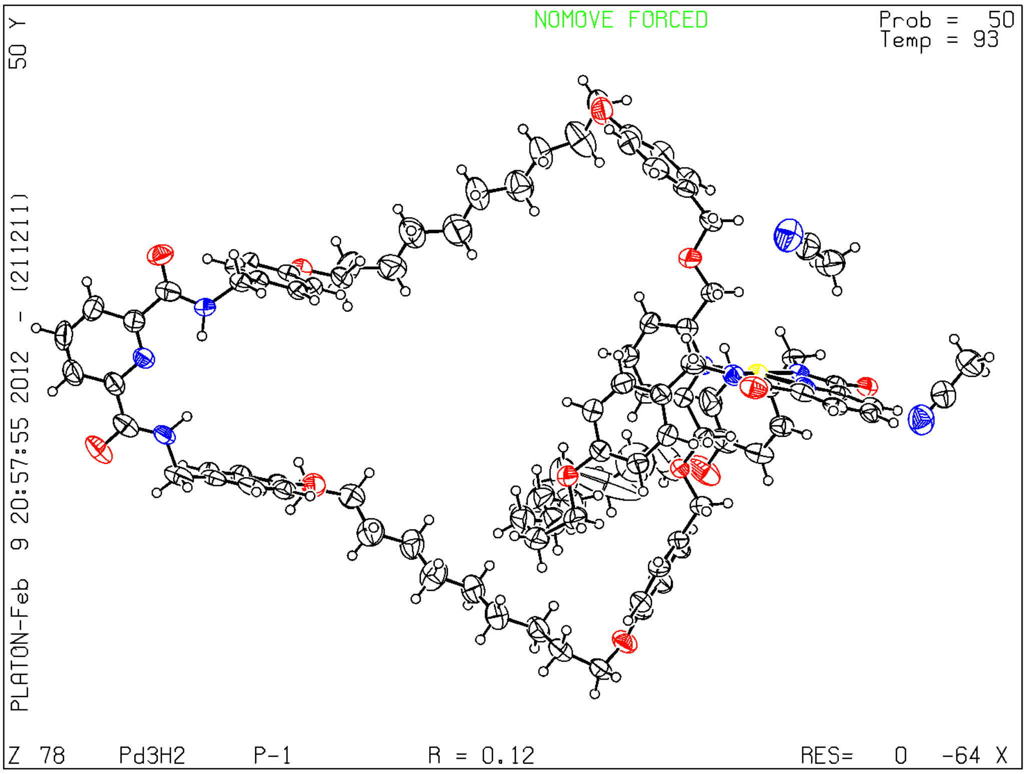


Figure S9. X-ray crystal structure of Pd**3**H_2

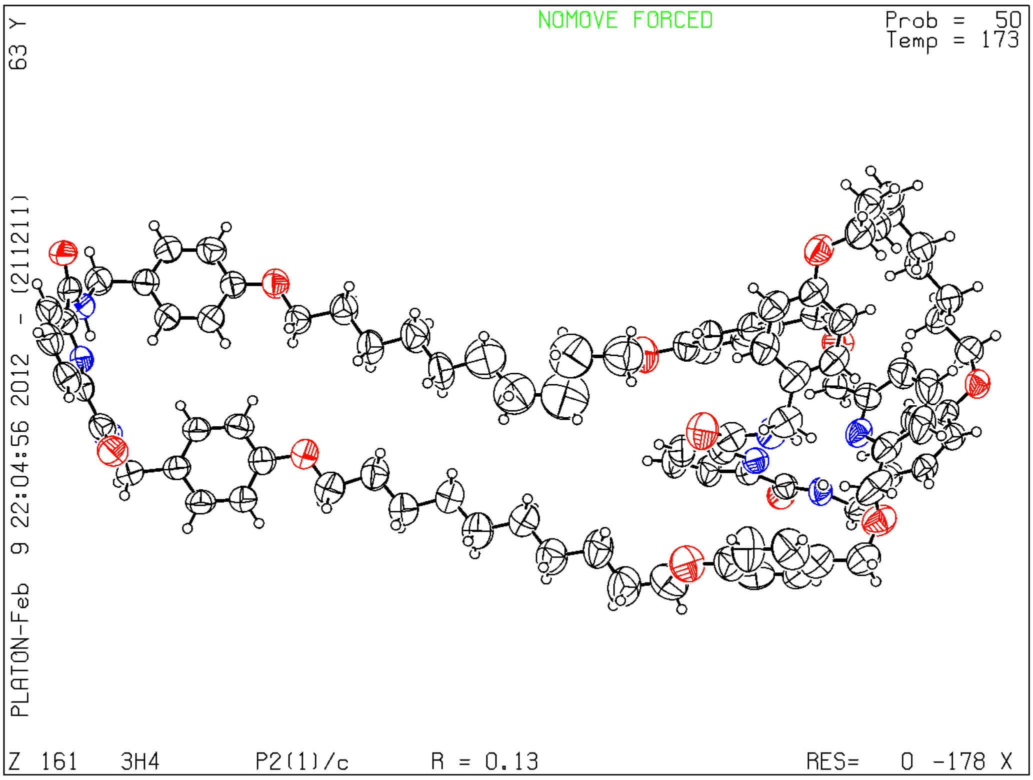


Figure S10. X-ray crystal structure of **3**H_4

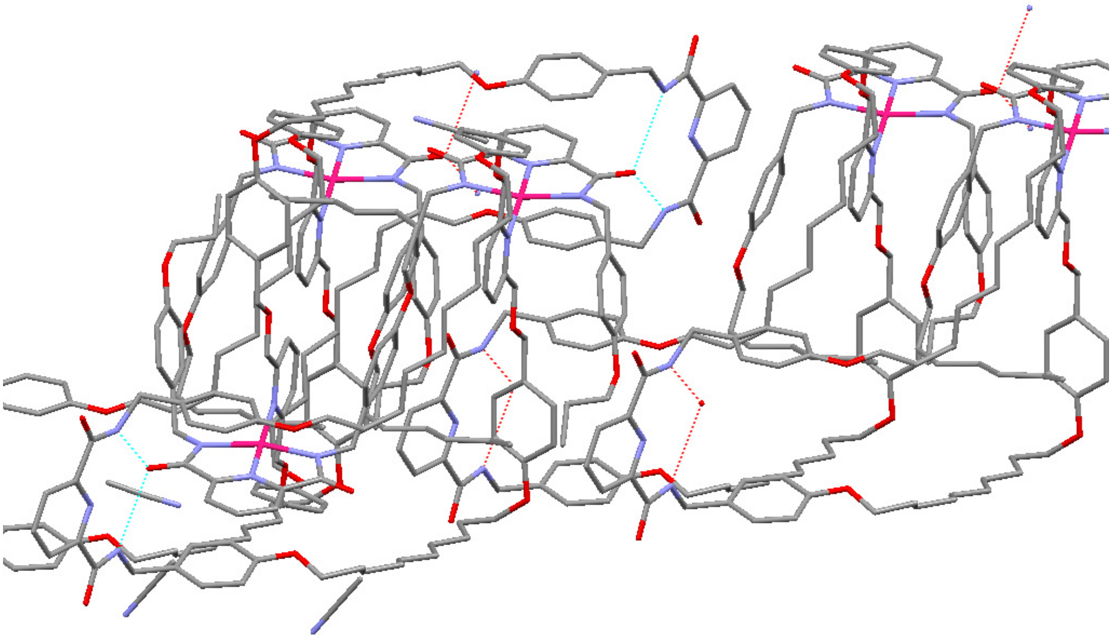


Figure S11. Crystal Packing of Pd**3**H_2

4. Mass Spectrometry Data

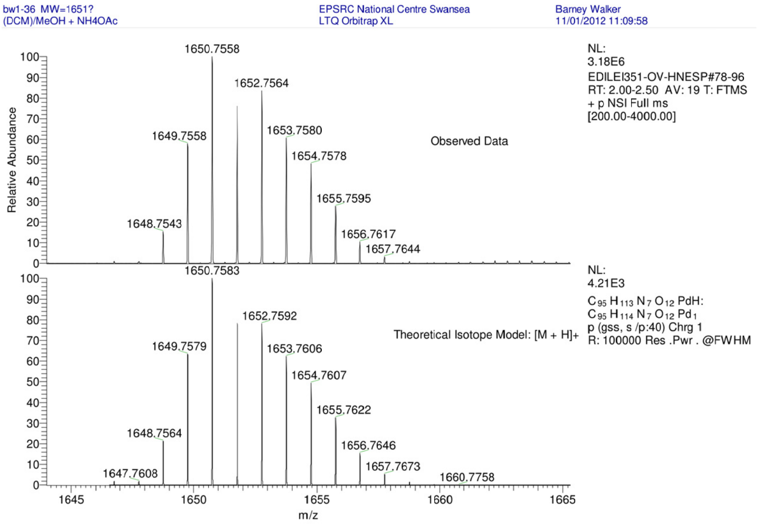


Figure S12. Mass Spectrum (+ESI) of **2**Pd(**1**H_2).

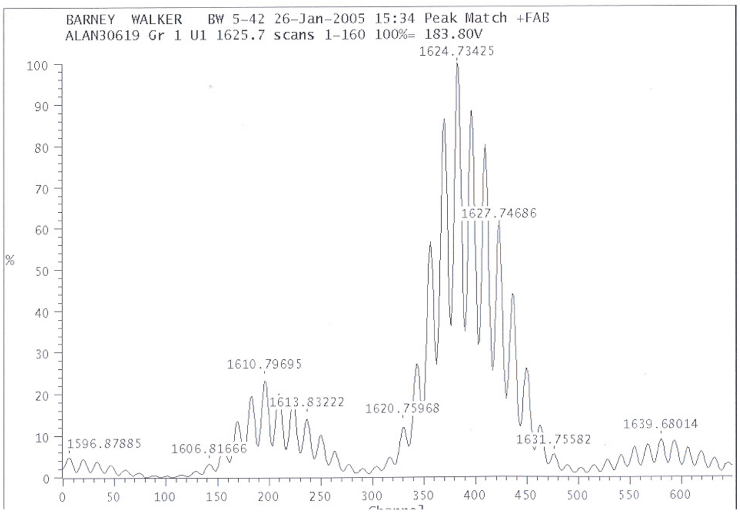


Figure S13. Mass Spectrum (+FAB) of Pd**3**H_2.

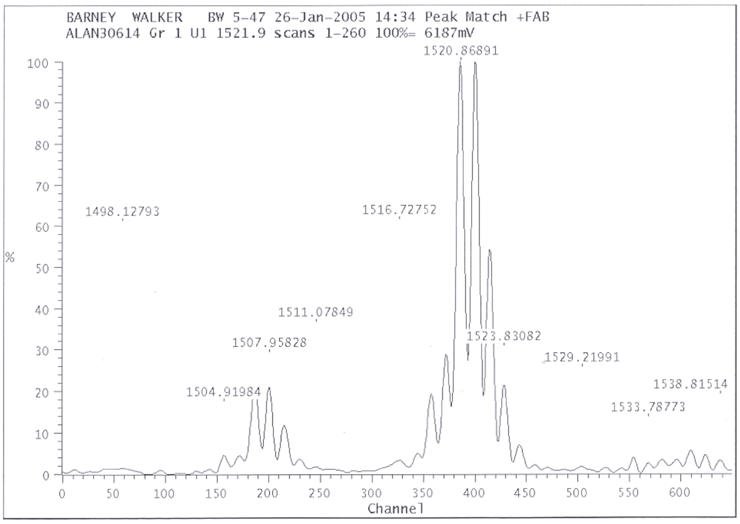
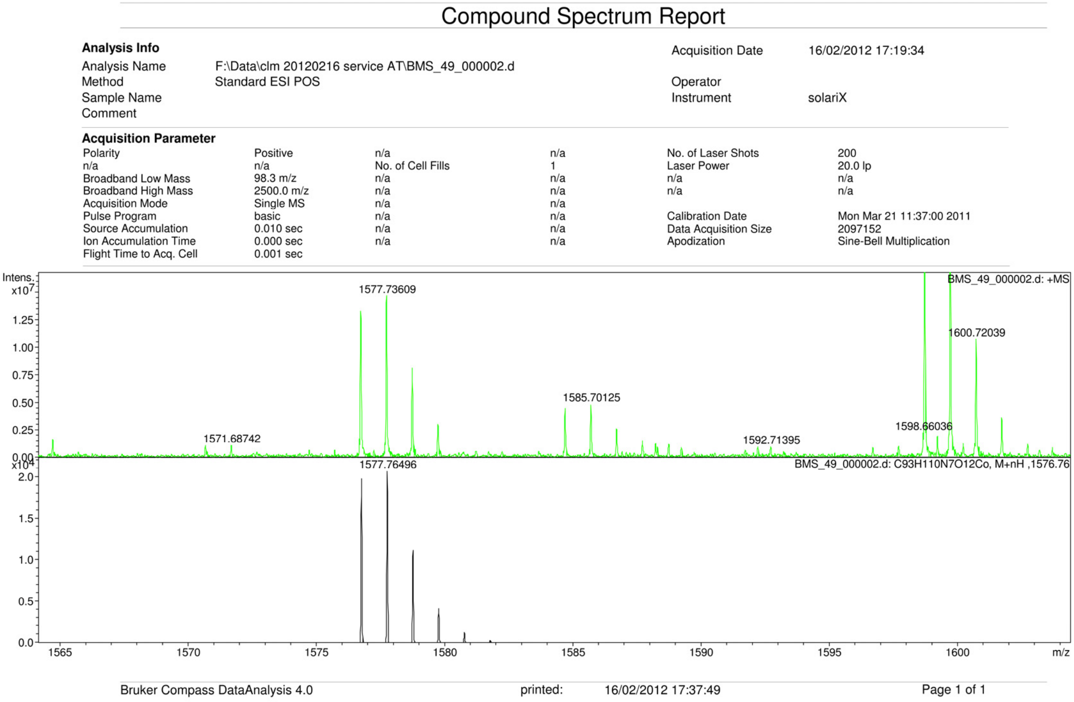


Figure S14. Mass Spectrum (+FAB) of **3**H_4.



Compound Spectrum Report

Analysis Info

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Method	Standard ESI POS	Operator	
Sample Name		Instrument	solariX
Comment			

Acquisition Parameter

Polarity	Positive	n/a	n/a	No. of Laser Shots	200
n/a	n/a	No. of Cell Fills	1	Laser Power	20.0 lp
Broadband Low Mass	98.3 m/z	n/a	n/a	n/a	n/a
Broadband High Mass	2500.0 m/z	n/a	n/a	n/a	n/a
Acquisition Mode	Single MS	n/a	n/a		
Pulse Program	basic	n/a	n/a	Calibration Date	Mon Mar 21 11:37:00 2011
Source Accumulation	0.010 sec	n/a	n/a	Data Acquisition Size	2097152
Ion Accumulation Time	0.000 sec	n/a	n/a	Apodization	Sine-Bell Multiplication
Flight Time to Acq. Cell	0.001 sec				

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Figure S15. Mass Spectrum (+ESI) of [Co**3**]NEt_4 showing M+ and [MHNa]+ peaks. Under the ESI acquisition conditions the complex appears to regain one proton and then fly as the sodium salt.