

## Anion complexation via C-H...X interactions using a palladacyclic receptor

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### I. Synthesis.

Complex **1** was prepared according to literature methods.<sup>1</sup>

**Complex 2a.** Complex **1** (1.137 g, 0.77 mmol) and 1,4,7-trithiacyclononane (0.260 g, 1.44 mmol) were dissolved in CH<sub>2</sub>Cl<sub>2</sub> (20 ml) then stirred at r.t. for 1 h. The solvent was removed under reduced pressure to give a crude yellow crystalline solid which was recrystallized from Et<sub>2</sub>O. Yield: 1.24 g (89 %). Anal. Calcd for C<sub>48</sub>H<sub>74</sub>ClO<sub>3</sub>PPdS<sub>3</sub>: C, 59.48 %; H, 7.70 %. Found: C, 59.46 %; H, 8.15 %. <sup>31</sup>P{<sup>1</sup>H} NMR (C<sub>6</sub>D<sub>6</sub>, 121.5 MHz, 298K): δ 135.2 (s). <sup>1</sup>H NMR (C<sub>6</sub>D<sub>6</sub>, 300 MHz, 298K): 1.10 (s, 9H, C(CH<sub>3</sub>)<sub>3</sub> o-metallated ring), 1.20 (s, 9H, C(CH<sub>3</sub>)<sub>3</sub> o-metallated ring), 1.21 (s, 18H, C(CH<sub>3</sub>)<sub>3</sub> free ring) 1.34 (s, 18H, C(CH<sub>3</sub>)<sub>3</sub> free ring), 2.48 (m, 6H, SCHHCHHS, *exo*), 3.55 (m, 6H, SCHHCHHS, *endo*), 6.68 (br d, 1H, J<sub>HH</sub> = 5 Hz, Ar-H), 7.10 (d, 2H, J<sub>HH</sub> = 5 Hz, Ar-H), 7.13 (d, 1H, J<sub>HH</sub> = 2 Hz, Ar-H), 7.21 (s, 1H, Ar-H), 7.23 (s, 1H, Ar-H), 7.36 (d, 2H, J<sub>HH</sub> = 2 Hz, Ar-H). <sup>13</sup>C{<sup>1</sup>H} NMR (CDCl<sub>3</sub>, 75 MHz, 248K): 29.8 (s, <sup>t</sup>Bu CH<sub>3</sub>), 30.7 (s, <sup>t</sup>Bu CH<sub>3</sub>), 31.8 (s, <sup>t</sup>Bu CH<sub>3</sub>), 32.1 (s, <sup>t</sup>Bu CH<sub>3</sub>), 34.0 (s, SCH<sub>2</sub>), 35.1 (s, C(CH<sub>3</sub>)<sub>3</sub>), 35.4 (s, C(CH<sub>3</sub>)<sub>3</sub>), 35.5 (s, C(CH<sub>3</sub>)<sub>3</sub>), 35.6 (s, C(CH<sub>3</sub>)<sub>3</sub>), 120.1 (s, Ar CH), 120.3 (s, Ar CH), 123.0 (s, Ar CH), 124.2 (s, Ar CH), 125.4 (s, Ar CH), 131.2 (d, J<sub>PC</sub> = 5 Hz, Ar C), 134.4 (s, Ar C), 134.9 (s, Ar C), 139.9 (d, J<sub>PC</sub> = 6 Hz, Ar C), 146.7 (s, Ar C), 147.8 (d, J<sub>PC</sub> = 6 Hz, Ar C), 148.8 (s, Ar C).

**Complex 2b.** Complex **1** (0.678 g, 0.70 mmol) was dissolved in CH<sub>2</sub>Cl<sub>2</sub> (10 ml), Ag[SbF<sub>6</sub>] (0.240 g, 0.70 mmol) was added and the mixture was stirred at r.t. for 1 h.

The solution was filtered through Celite to remove precipitated AgCl and the solvent removed under reduced pressure to give a grey solid. The crude product was recrystallized by slow evaporation of a conc. hexane solution. Yield: 0.650 g (79 %). Crystals of **2b** suitable for X-ray analysis were grown from a conc. benzene solution. Anal. Calcd for C<sub>48</sub>H<sub>74</sub>F<sub>6</sub>O<sub>3</sub>PPdS<sub>3</sub>Sb: C, 49.32 %; H, 6.38 %. Found: C, 49.62 %; H, 6.64 %. <sup>31</sup>P{<sup>1</sup>H} NMR (CDCl<sub>3</sub>, 121.5 MHz): δ 130.7 (s). <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz): 1.17 (s, 9H, C(CH<sub>3</sub>)<sub>3</sub> o-metallated ring), 1.27 (s, 9H, C(CH<sub>3</sub>)<sub>3</sub> o-metallated ring), 1.28 (s, 18H, C(CH<sub>3</sub>)<sub>3</sub> free ring), 1.41 (s, 18H, C(CH<sub>3</sub>)<sub>3</sub> free ring), 2.60 (m, 6H, SCHHCHHS, *exo*), 2.98 (m, 6H, SCHHCCHHS, *endo*), 6.71 (dd, 1H, J<sub>HH</sub> = 4 & 8 Hz, Ar-H o-metallated ring), 7.13 (d, 1H, J<sub>HH</sub> = 4 Hz, Ar-H), 7.14 (d, 2H, J<sub>HH</sub> = 4 Hz, Ar-H), 7.23 (d, 1H, J<sub>HH</sub> = 4 Hz, Ar-H), 7.27 (d, 1H, J<sub>HH</sub> = 4 Hz, Ar-H), 7.35 (m, 2H, Ar-H). <sup>13</sup>C{<sup>1</sup>H} NMR (CDCl<sub>3</sub>, 75 MHz): 29.8 (s, <sup>t</sup>Bu CH<sub>3</sub>), 30.8 (s, <sup>t</sup>Bu CH<sub>3</sub>), 31.8 (s, <sup>t</sup>Bu CH<sub>3</sub>), 32.1 (s, <sup>t</sup>Bu CH<sub>3</sub>), 33.1 (s, SCH<sub>2</sub>), 35.1 (s, C(CH<sub>3</sub>)<sub>3</sub>), 35.4 (s, C(CH<sub>3</sub>)<sub>3</sub>), 35.5 (s, C(CH<sub>3</sub>)<sub>3</sub>), 35.6 (s, C(CH<sub>3</sub>)<sub>3</sub>), 118.7 (s, Ar CH), 118.8 (s, Ar CH), 121.9 (s, Ar CH), 123.1 (s, Ar CH), 124.1 (s, Ar CH), 129.6 (d, J<sub>PC</sub> = 5 Hz, Ar C), 134.3 (s, Ar C), 134.6 (s, Ar C), 138.4 (d, J<sub>PC</sub> = 6 Hz, Ar C), 145.2 (s, Ar C), 146.4 (d, J<sub>PC</sub> = 6 Hz, Ar C), 147.5 (s, Ar C). HRMS (ESI) [M]<sup>+</sup> Calcd for C<sub>48</sub>H<sub>74</sub>F<sub>6</sub>O<sub>3</sub>PPdS<sub>3</sub>Sb: 1166.2515. Found: 1166.2531. [M-SbF<sub>6</sub>]<sup>+</sup> Calcd: 931.3573. Found: 931.3588.

**Complex 2c.** Complex **1** (0.124 g, 0.128 mmol) was dissolved in CH<sub>2</sub>Cl<sub>2</sub> (5 ml), [NH<sub>4</sub>][PF<sub>6</sub>] (0.021 g, 0.128 mmol) was added and the mixture was stirred at r.t. for 1 h. The solution was filtered through Celite to remove precipitated [NH<sub>4</sub>]Cl and the solvent removed under reduced pressure to give a pale yellow solid. Yield: 0.121 g (88 %). Anal. Calcd for C<sub>48</sub>H<sub>74</sub>F<sub>6</sub>O<sub>3</sub>P<sub>2</sub>PdS<sub>3</sub>: C, 53.50 %; H, 6.92 %. Found: C, 54.17 %; H, 7.26 %. <sup>31</sup>P{<sup>1</sup>H} NMR (CDCl<sub>3</sub>, 121.5 MHz): δ 130.8 (s), -143.1 (heptet, J<sub>FP</sub> =

710 Hz,  $\text{PF}_6$ ).  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 300 MHz): 1.16 (s, 9H,  $\text{C}(\underline{\text{CH}}_3)_3$  o-metallated ring), 1.26 (s, 9H,  $\text{C}(\underline{\text{CH}}_3)_3$  o-metallated ring), 1.27 (s, 18H,  $\text{C}(\underline{\text{CH}}_3)_3$  free ring), 1.41 (s, 18H,  $\text{C}(\underline{\text{CH}}_3)_3$  free ring), 2.59 (m, 6H,  $\text{SCH}\underline{\text{H}}\text{C}\underline{\text{H}}\text{HS}$ , *exo*), 2.97 (m, 6H,  $\text{SCH}\underline{\text{H}}\text{C}\underline{\text{H}}\text{HS}$ , *endo*), 6.71 (br d, 1H,  $J_{\text{HH}} = 6$  Hz, Ar- $\underline{\text{H}}$  o-metallated ring), 7.11 (d, 1H,  $J_{\text{HH}} = 3$  Hz, Ar- $\underline{\text{H}}$ ), 7.14 (d, 2H,  $J_{\text{HH}} = 3$  Hz, Ar- $\underline{\text{H}}$ ), 7.23 (d, 1H,  $J_{\text{HH}} = 3$  Hz, Ar- $\underline{\text{H}}$ ), 7.25 (d, 1H,  $J_{\text{HH}} = 3$  Hz, Ar- $\underline{\text{H}}$ ), 7.41 (br s, 2H, Ar- $\underline{\text{H}}$ ).  $^{13}\text{C}\{^1\text{H}\}$  NMR ( $\text{CDCl}_3$ , 75 MHz): 29.8 (s,  $^t\text{Bu}$   $\underline{\text{C}}\text{H}_3$ ), 30.7 (s,  $^t\text{Bu}$   $\underline{\text{C}}\text{H}_3$ ), 31.8 (s,  $^t\text{Bu}$   $\underline{\text{C}}\text{H}_3$ ), 32.1 (s,  $^t\text{Bu}$   $\underline{\text{C}}\text{H}_3$ ), 33.0 (s,  $\text{S}\underline{\text{C}}\text{H}_2$ ), 35.1 (s,  $\underline{\text{C}}(\text{CH}_3)_3$ ), 35.4 (s,  $\underline{\text{C}}(\text{CH}_3)_3$ ), 35.5 (s,  $\underline{\text{C}}(\text{CH}_3)_3$ ), 35.6 (s,  $\underline{\text{C}}(\text{CH}_3)_3$ ), 120.1 (s, Ar  $\underline{\text{C}}\text{H}$ ), 120.2 (s, Ar  $\underline{\text{C}}\text{H}$ ), 123.3 (s, Ar  $\underline{\text{C}}\text{H}$ ), 124.5 (s, Ar  $\underline{\text{C}}\text{H}$ ), 125.5 (s, Ar  $\underline{\text{C}}\text{H}$ ), 131.1 (d,  $J_{\text{PC}} = 5$  Hz, Ar  $\underline{\text{C}}$ ), 134.4 (s, Ar  $\underline{\text{C}}$ ), 134.9 (s, Ar  $\underline{\text{C}}$ ), 139.9 (d,  $J_{\text{PC}} = 6$  Hz, Ar  $\underline{\text{C}}$ ), 146.6 (s, Ar  $\underline{\text{C}}$ ), 147.9 (d,  $J_{\text{PC}} = 6$  Hz, Ar  $\underline{\text{C}}$ ), 148.9 (s, Ar  $\underline{\text{C}}$ ). HRMS (EI)  $[\text{M-PF}_6]^+$  Calcd for  $\text{C}_{48}\text{H}_{74}\text{O}_3\text{PPdS}_3$ : 931.3573. Found: 931.3601.

**Complex 3.** Complex **1** (0.101 g, 0.032 mmol) was dissolved in  $\text{CH}_2\text{Cl}_2$  (10 ml),  $[\text{Bu}_4\text{N}]\text{Cl}$  (0.036 g, 0.128 mmol) was added and the mixture stirred at r.t. for 1 h. The solution was filtered through Celite and then the solvent removed under reduced pressure to give a crude yellow solid. Repeated recrystallisation of the crude product mixture from  $\text{CH}_2\text{Cl}_2:\text{Et}_2\text{O}$  gave impure **3** contaminated with  $[\text{Bu}_4\text{N}]\text{Cl}$ .  $^{31}\text{P}\{^1\text{H}\}$  NMR ( $\text{CDCl}_3$ , 121.5 MHz):  $\delta$  124.0 (s).  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 300 MHz): 0.89 (t, 12H,  $J_{\text{HH}} = 6$  Hz,  $\underline{\text{C}}\text{H}_3$ ), 1.08 (s, 9H,  $\text{C}(\underline{\text{CH}}_3)_3$  o-metallated ring), 1.18 (s, 27H,  $\text{C}(\underline{\text{CH}}_3)_3$ ), 1.25 (s, 18H,  $\text{C}(\underline{\text{CH}}_3)_3$  free ring), 1.37 (m, 8H,  $\underline{\text{C}}\text{H}_2$ ), 1.58 (m, 8H,  $\underline{\text{C}}\text{H}_2$ ), 3.27 (m, 8H,  $\underline{\text{C}}\text{H}_2$ ), 6.93 (d, 2H,  $J_{\text{HH}} = 3$  Hz, Ar- $\underline{\text{H}}$ ), 6.96 (d, 1H,  $J_{\text{HH}} = 3$  Hz, Ar- $\underline{\text{H}}$ ), 7.24 (d, 2H,  $J_{\text{HH}} = 3$  Hz, Ar- $\underline{\text{H}}$ ), 7.75 (dd, 2H,  $J_{\text{HH}} = 7$  Hz,  $J_{\text{HH}} = 3$  Hz, Ar- $\underline{\text{H}}$ ), 8.19 (dd, 1H,  $J_{\text{HH}} = 7$  Hz,  $^4J_{\text{HH}} = 3$  Hz, Ar- $\underline{\text{H}}$ ).  $^{13}\text{C}\{^1\text{H}\}$  NMR ( $\text{CDCl}_3$ , 75 MHz): 14.1 (s,  $\underline{\text{C}}\text{H}_3$ ), 20.1 (s,  $\underline{\text{C}}\text{H}_2$ ), 24.6 (s,  $\underline{\text{C}}\text{H}_2$ ), 30.2 (s,  $^t\text{Bu}$   $\underline{\text{C}}\text{H}_3$ ), 30.7 (s,  $^t\text{Bu}$   $\underline{\text{C}}\text{H}_3$ ), 31.8 (s,  $^t\text{Bu}$   $\underline{\text{C}}\text{H}_3$ ), 32.3 (s,

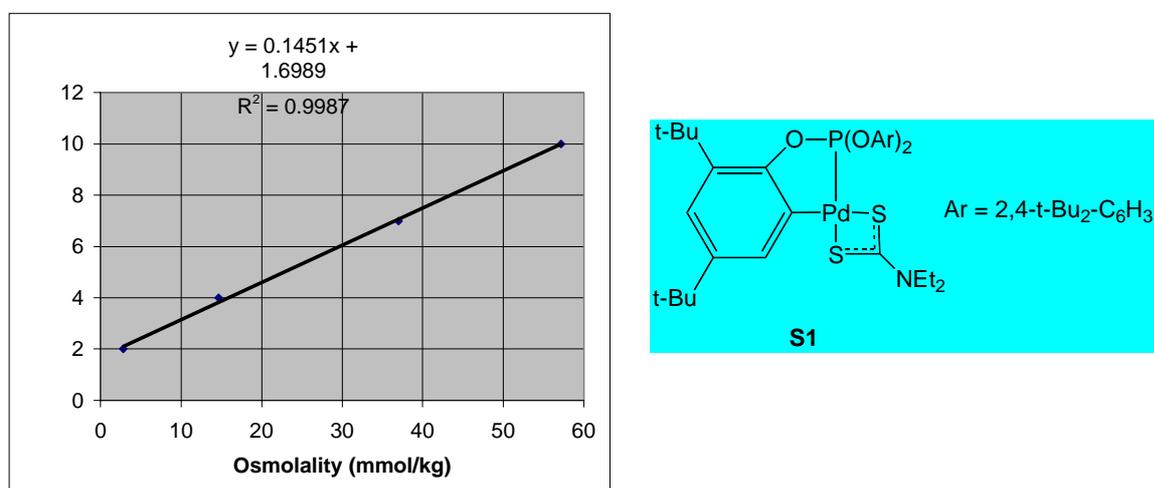
<sup>1</sup>Bu CH<sub>3</sub>), 34.8 (s, C(CH<sub>3</sub>)<sub>3</sub>), 35.2 (s, C(CH<sub>3</sub>)<sub>3</sub>), 35.3 (s, C(CH<sub>3</sub>)<sub>3</sub>), 35.4 (s, C(CH<sub>3</sub>)<sub>3</sub>), 59.4 (s, NCH<sub>2</sub>), 120.4 (s, Ar CH), 120.6 (s, Ar CH), 121.3 (s, Ar CH), 124.1 (s, Ar CH), 124.4 (s, Ar CH), 125.0 (s, Ar C), 132.3 (d, *J*<sub>PC</sub> = 6 Hz, Ar C), 139.1 (d, *J*<sub>PC</sub> = 10 Hz, Ar C), 144.4 (s, Ar C), 146.3 (d, *J*<sub>PC</sub> = 6 Hz, Ar C), 148.8 (s, Ar C), 152.0 (s, Ar C).

**Complex 2d.** Complex **1** (0.200 g, 0.127 mmol) and 1,4,7-trithiacyclononane (0.023 g, 0.127 mmol) were dissolved in benzene (5 ml) and the solution was stirred at r.t. for 2 h. After this time the solvent was removed under reduced pressure to give a crystalline yellow solid. Yield: 0.245 g (96 %). Crystals of **2d** suitable for X-ray analysis were grown from a concentrated Et<sub>2</sub>O solution. Anal. Calcd for C<sub>90</sub>H<sub>136</sub>Cl<sub>2</sub>O<sub>6</sub>P<sub>2</sub>Pd<sub>2</sub>S<sub>3</sub>: C, 61.56 %; H, 7.81 %. Found: C, 61.52 %; H, 8.01 %. Peaks in <sup>1</sup>H and <sup>31</sup>P{<sup>1</sup>H} NMR spectra marked with \* correspond to the anionic complex. <sup>31</sup>P{<sup>1</sup>H} NMR (C<sub>6</sub>D<sub>6</sub>, 121.5 MHz): δ 135.3 (s), 126.9\* (s). <sup>1</sup>H NMR (C<sub>6</sub>D<sub>6</sub>, 300 MHz): 1.05\* (s, 18H, C(CH<sub>3</sub>)<sub>3</sub>), 1.07 (s, 18H, C(CH<sub>3</sub>)<sub>3</sub>), 1.11\* (s, 9H, C(CH<sub>3</sub>)<sub>3</sub> o-metallated ring), 1.23 (s, 9H, C(CH<sub>3</sub>)<sub>3</sub> o-metallated ring), 1.38\* (s, 9H, C(CH<sub>3</sub>)<sub>3</sub> o-metallated ring), 1.40\* (s, 18H, C(CH<sub>3</sub>)<sub>3</sub>), 1.43 (s, 9H, C(CH<sub>3</sub>)<sub>3</sub> o-metallated ring), 1.71 (s, 18H, C(CH<sub>3</sub>)<sub>3</sub>), 2.06 (m, 6H, SCHHCHHS, *exo*), 3.51 (m, 6H, SCHHCHHS, *endo*), 6.60 (dt, 4H [2H\*], *J*<sub>HH</sub> = 3 & 8 Hz, Ar-H), 6.92 (d, 1H, *J*<sub>HH</sub> = 5 Hz, Ar-H), 7.25 (br s, 1H, Ar-H), 7.31\* (br d, 2H, *J*<sub>HH</sub> = 9 Hz, Ar-H), 7.35 (br s, 2H, Ar-H), 7.39\* (br s, 1H, Ar-H), 7.44\* (br s, 2H, Ar-H), 8.24 (br d, 2H, *J*<sub>HH</sub> = 9 Hz, Ar-H), 9.30\* (br d, 1H, *J*<sub>HH</sub> = 3 Hz, Ar-H). <sup>13</sup>C{<sup>1</sup>H} NMR (CDCl<sub>3</sub>, 75 MHz): 29.9, 30.1, 30.7, 31.8, 31.9, 32.1, 32.2, 33.2, 34.9, 35.2, 35.3, 35.4, 35.5, 35.6, 118.7, 118.8, 120.4, 120.6, 121.9, 122.0, 124.1, 124.2, 124.4, 125.0, 129.4, 129.5, 132.3, 132.4, 134.3, 134.6,

138.3, 138.4, 139.1, 144.3, 144.4, 144.5, 145.2, 146.4, 146.5, 147.4, 147.5, 148.8,  
152.0.

## II. Vapour Pressure Osmometry experiment on complex **2d**.

A Vapro 5520 vapour pressure osmometer (manufacturer: Wescor) was used for molecular weight determination. So that organic solvents could be used, the instrument response at 298K was calibrated in benzene for compound **S1** for known concentrations (M).<sup>1</sup> The calibration graph is shown below.



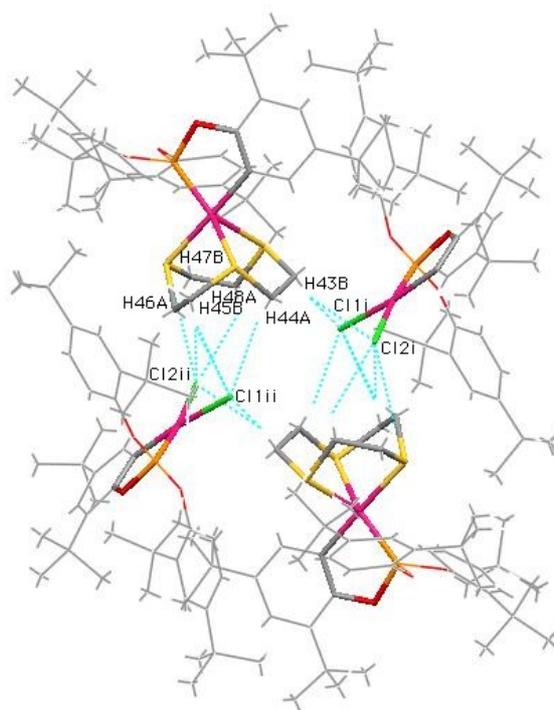
**Figure S1.** VPO calibration with compound **S1**.

Compound **2d** (0.053 g, 0.030 mmol) was dissolved in C<sub>6</sub>H<sub>6</sub> (5 ml) ([**2d**] = 6.0 mM). An instrument reading of 35.88 (±2.0) was measured, giving an observed concentration of 6.90 (±0.2) mM, corresponding to an average molecular weight consistent with a dimeric (rather than a tetrameric) structure in solution.

## II. X-ray Crystallography

### (a) Complex 2d (CCDC number: 662915)

$C_{42}H_{63}Cl_2O_3PPd$ ,  $C_{48}H_{74}O_3PPdS_3$ ,  $CD_3CN$ ,  $\lambda = 0.71073 \text{ \AA}$ , space group =  $P-1$ ,  $a = 15.297(4) \text{ \AA}$ ,  $b = 18.455(4) \text{ \AA}$ ,  $c = 19.724(7) \text{ \AA}$ ,  $\alpha = 108.554(19)^\circ$ ,  $\beta = 107.430(19)^\circ$ ,  $\gamma = 98.853(15)^\circ$ ,  $V = 4842(2) \text{ \AA}^3$ ,  $Z = 2$ ,  $\mu = 0.572 \text{ mm}^{-1}$ , 36518 data were collected of which 21041 were independent. The structure was refined on  $F^2$  to give  $R1 = 0.0549$  ( $F^2 > 2\sigma F^2$ ) and  $wR2$  (all data) = 0.1259.



**Figure S2.** X-ray structure of complex **2d**.

D	H	A	D...A	H...A	D-H...A
C43	H43B	C11 <sup>i</sup>	3.478(9)	2.55	156
C44	H44A	C11 <sup>ii</sup>	3.566(7)	2.70	146
C46	H46A	C11 <sup>ii</sup>	3.464(7)	2.78	126
C45	H45B	C11 <sup>ii</sup>	3.596(7)	2.95	124
C43	H43B	C12 <sup>i</sup>	3.450(8)	2.84	120

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C47	H47B	C12 <sup>ii</sup>	3.575(6)	2.87	128
C48	H48A	C12 <sup>ii</sup>	3.510(7)	2.87	123
C46	H46A	C12 <sup>ii</sup>	3.730(8)	2.94	137

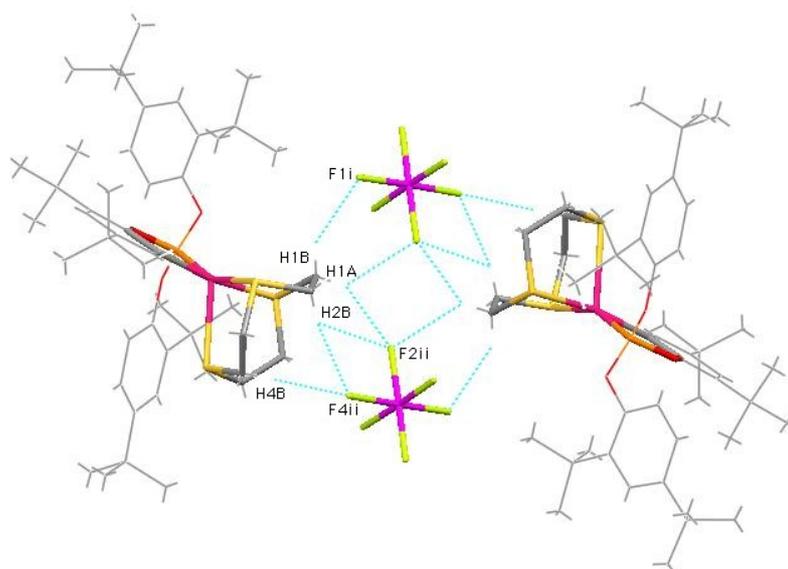
Symmetry operations:

$$^i = x-1, y, z$$

$$^{ii} = -x, -y+1, -z+1$$

**(b) Complex 2b (CCDC number: 662914)**

$C_{42}H_{68}O_3PPdS_3 \cdot 4C_6H_6 \cdot SbF_6$ ,  $\lambda = 0.71073 \text{ \AA}$ , space group =  $P-1$ ,  $a = 12.32(2) \text{ \AA}$ ,  $b = 12.719(13) \text{ \AA}$ ,  $c = 22.10(5) \text{ \AA}$ ,  $\alpha = 83.91(11)^\circ$ ,  $\beta = 79.8(2)^\circ$ ,  $\gamma = 78.56(8)$ ,  $V = 3332(10) \text{ \AA}^3$ ,  $Z = 2$ ,  $\mu = 0.853 \text{ mm}^{-1}$ , 73574 data were collected of which 15255 were independent. The structure was refined on  $F^2$  to give  $R1 = 0.0757$  ( $F^2 > 2\sigma F^2$ ) and  $wR2$  (all data) = 0.1868.



**Figure S3.** X-ray structure of complex **2b**.

**D H A D...A H...A D-H...A**

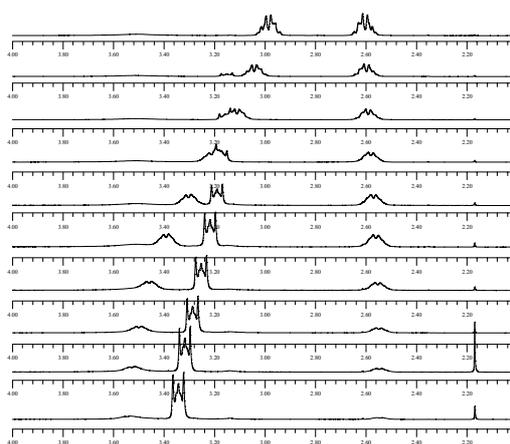
C1	H1B	F1 <sup>i</sup>	3.300(10)	2.45	144
C1	H1A	F2 <sup>ii</sup>	3.193(11)	2.48	128
C2	H2B	F2 <sup>ii</sup>	3.152(10)	2.58	117
C2	H2B	F4 <sup>ii</sup>	3.494(11)	2.54	162
C4	H4B	F4 <sup>ii</sup>	3.309(11)	2.44	146
C6	H6B	F2 <sup>ii</sup>	3.608(12)	2.80	139

Symmetry operations:

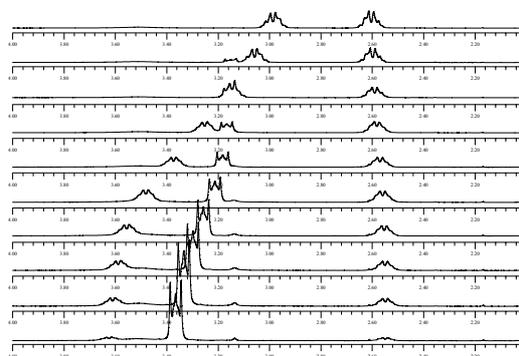
$$^i = x, y, 1+z$$

$$^{ii} = 1+x, 1+y, 2+z$$

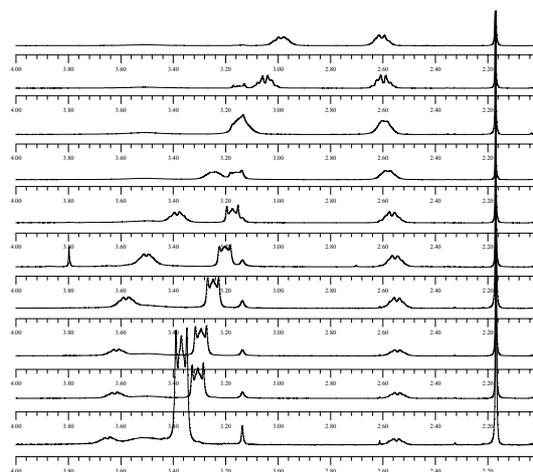
#### IV. NMR Binding studies with halide salts in CDCl<sub>3</sub>



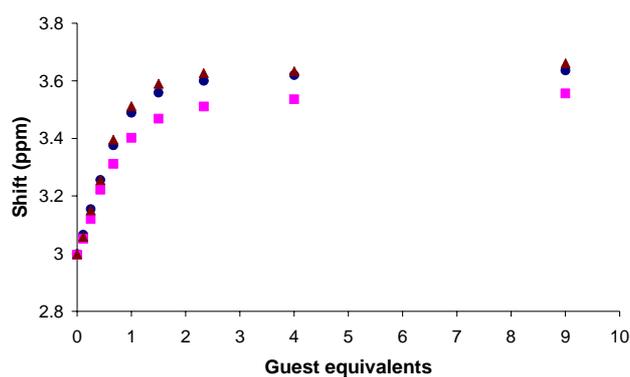
**Figure S4.** (a) <sup>1</sup>H NMR spectra of **2b** and TBA-I in various ratios at 5.07 mM total concentration.



**Figure S4.** (b) <sup>1</sup>H NMR spectra of **2b** and TBA-Br in various ratios at 5.17 mM total concentration.



**Figure S4.** (c)  $^1\text{H}$  NMR spectra of **2b** and TBA-Cl in various ratios at 4.75 mM total concentration.



**Figure S5.** Representation of NMR data in Figure S4 as titrations of molar equivalents of guest against  $\delta$  value of *endo* proton on **2b** (blue = bromide, pink = iodide, brown = chloride)

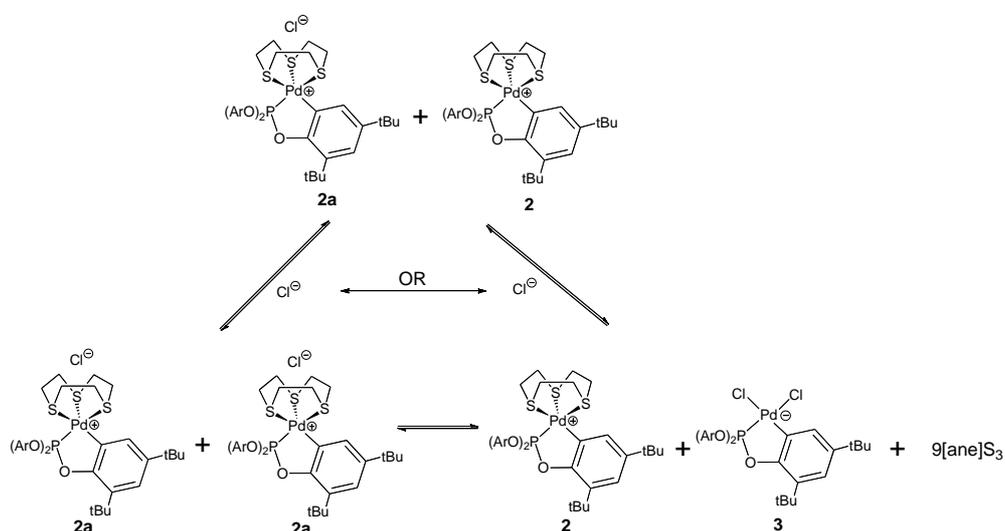
Binding data were fitted using the program WinEqNMR<sup>3</sup> giving the following values:

**2b** + TBA-Cl:  $\text{Log}K = 3.70 (\pm 0.07)$  – see text below

**2b** + TBA-Br:  $\text{Log}K = 3.57 (\pm 0.04)$  – see text below

**2b** + TBA-I:  $\text{Log}K = 3.34 (\pm 0.05)$

The three binding constants give acceptable error values and bear out the trend observed by inspection of the titration curves. However it is difficult to quantify to what extent the appearance of free macrocycle (at 3.14 ppm) during the titrations with chloride and bromide affects these values. Nevertheless, it is likely that if anything, this process lowers the observed values since a competition is set up between the guest binding the metal directly and binding the free receptor, as illustrated in Scheme S1 below for the case of chloride.



**Scheme S1.** Equilibria that would account for the formation of the free macrocycle 9[ane]S<sub>3</sub> and complexes **2a** and **3** in CDCl<sub>3</sub> solution upon addition of chloride to **2** (SbF<sub>6</sub> salt of **2** = **2b**)

## References

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