A di-palladium urea complex as molecular receptor for anions

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Supplementary Information

Synthesis

Materials and Apparatus. All manipulations were carried out in an atmosphere of purified and dry dinitrogen using standard Schlenk line techniques unless otherwise stated. Solvents were dried from the appropriate drying agent, degassed and stored under nitrogen. All commercially available starting materials were not further purified unless otherwise stated. ^{1}H, ^{31}P, and ^{13}C NMR spectra were recorded on either a JEOL-EX270 or a Bruker Avance 400 Ultrashield NMR spectrometer (270.17 MHz, 109.38 MHz, 67.94 MHz respectively) with TMS, H_3PO_4 and TMS respectively as internal references. IR spectra were recorded on Research Series FT-IR using KBr disks in the range 4000-500 cm^{-1}. Pd(dppp)Cl_2 and Pd(dppp)$(OTf)_2$ were synthesized by adaptation of previously reported procedures.[1,2]

Synthesis of [$C_6H_5NHC(=O)NH(CH_2)_2S$-]$_2$ (1). [-$S(CH_2)_2NH_2]_2\cdot 2HCl$ (2.252 g, 10 mmol) and K_2CO_3 (6.219 g, 45 mmol) were suspended in dry MeCN (60 ml) under a dinitrogen atmosphere; this was followed by addition of C_6H_5NCO (2.4 ml, 22 mmol). The reaction mixture was refluxed gently overnight. After allowing the mixture to cool down to room temperature a white solid precipitated which was filtered and washed with H_2O (2 x 50 ml) and Et_2O (2 x 50 ml) to afford the final product as a white powder. Yield: 2.915 g, 75 %. Elemental Analysis Found: C, 55.48; H, 5.65; N, 14.59. Calculated for $C_{18}H_{22}N_4O_2S_2$: C, 55.36; H, 5.68; N, 14.35. IR (ν (KBr)): 3334, 3307 (N-H), 3193, 3145, 3037, 2940 (C-H), 1645, 1597 (C=O), 1574, 1498 (arom.), 696 (C-S). FAB(+)-MS m/z: 391 (67%), $[M]^+$; 195 (47%), $[C_6H_5NHCONH(CH_2)_2S]^+$, 163 (26%), $[C_6H_5NHCONH(CH_2)_2]^+$. ^1H NMR (dmso-d_6): $\delta = 8.57$ (s, 2H, NH), 7.38 (d, 4H, *o*-ArH, $^3J_{o-m} = 7.7$ Hz), 7.21 (dd, 4H, *m*-ArH, $^3J_{o-m} = 7.7$ Hz, $^3J_{m-p} = 8.0$ Hz), 6.89 (t, 2H, *p*-ArH, $^3J_{p-m} = 8.0$ Hz), 6.35 (t, 2H, NH, $^3J_{\text{H-H}} = 5.7$ Hz), 3.41 (dt, 4H, CH_2CH_2S, $^3J_{\text{NH-H}} = 5.7$ Hz, $^3J_{\text{CH-H}} = 6.4$ Hz), 2.85 (t, 4H, CH_2S, $^3J_{\text{H-H}} = 6.4$ Hz). ^{13}C NMR (dmso-d_6): $\delta = 155.1$, 140.3, 128.6, 121.1, 117.7, 38.2, 38.0.

Synthesis of [$C_6H_5NHC(=O)NH(CH_2)_2S]_2Pb$ (2). Compound **1** (1.306 g, 3.4 mmol), triphenylphosphine (1.754, 6.7 mmol) and $HCl_{(aq)}$ 37% (2 drops) were suspended in a degassed mixture of 1,4-dioxane (50 ml) and H_2O (5 ml) and stirred overnight at reflux under nitrogen, to reduce the disulphide bond to the corresponding thiol. After allowing the reaction to cool down to ~40°C, $Pb(AcO)_2$ (1.269 g, 3.4 mmol) was added along with acetone (2 ml) to help it dissolve. A yellow precipitate formed within 20 min. The reaction mixture was stirred for one further hour before the yellow precipitate was filtered and washed with water (50 ml), acetone (50 ml) and diethyl ether (2 x 30 ml) to yield the final product. Yield: 1.689 g, 84 %. Elemental Analysis

Found: C, 36.06; H, 3.60; N, 9.24. Calculated for $C_{18}H_{22}N_4O_2PbS_2$: C, 36.17; H, 3.71; N, 9.37. IR (ν (KBr)): 3294 (N-H), 3109, 3057, 2900 (C-H), 1632 (C=O), 1574 (C=C.). FAB(+)-MS m/z: 596 (3%), $[M]^+$. ^{1}H NMR (dmso-d_6): δ = 8.53 (s, 2H, NH), 7.38 (d, 4H, *o*-ArH, $^3J_{H\text{-}H}$ = 7.7 Hz), 7.20 (dd, 4H, *m*-ArH, $^3J_{H\text{-}H}$ = 7.7 Hz, $^3J_{H\text{-}H}$ = 7.3 Hz), 6.87 (t, 2H, *p*-ArH, $^3J_{H\text{-}H}$ = 7.3 Hz), 6.24 (t, 2H, NH, $^3J_{\text{H-H}}$ = 5.4 Hz), 3.26 (dt, 4H, SCH_2CH_2, $^3J_{\text{NH-H}}$ = 5.4 Hz, $^3J_{\text{CH-H}}$ = 6.8 Hz), 3.55 (t, 4H, SCH_2, $^3J_{\text{H-H}}$ = 6.8 Hz). ^{13}C NMR (dmso-d_6): δ = 155.1, 140.3, 128.6, 121.1, 117.7, 45.0, 27.6.

Synthesis of $C_6H_5NHC(=O)NH(CH_2)_2SH$ (3). $Pb[S(CH_2)NHCONHC_6H_5]_2$ (0.597 g, 1.0 mmol) was suspended in MeOH (20 ml) and 10 ml of a 0.24 M solution of HCl (2.4 mmol) were added dropwise to the reaction. The reaction mixture changed from yellow-orange to white within 15 min. After 1.5 hrs the suspended solid was filtered off and rinsed with $CHCl_3$ (2 x 20 ml). The extracts were combined with the filtrate and evaporated under reduced pressure to dryness. The resulting white solid was washed with water (3 x 20 ml) to eliminate excess of acid. Yield: 0.345 g, 88 %. Elemental Analysis Found: C, 55.04; H, 6.29; N, 14.12. Calculated for $C_9H_{12}N_2OS$: C, 55.08; H, 6.16; N, 14.27. IR (ν (KBr)): 3313 (N-H), 3107, 3028, 2943 (C-H), 1639, 1593 (C=O), 1574 (arom.), 671 (C-S). FAB(+)-MS m/z: 197 (100%), $[M]^+$. ^{1}H NMR (dmso-d_6): δ = 8.52 (s, 1H, NH), 7.38 (d, 2H, *o*-ArH, $^3J_{H\text{-}H}$ = 7.6 Hz), 7.21 (dd, 2H, *m*-ArH, $^3J_{H\text{-}H}$ = 7.6 Hz, $^3J_{H\text{-}H}$ = 7.3 Hz), 6.89 (t, 1H, *p*-ArH, $^3J_{H\text{-}H}$ = 7.3 Hz), 6.32 (t, 1H, NH, $^3J_{\text{H-H}}$ = 5.4 Hz), 3.23 (dt, 2H, SCH_2CH_2, $^3J_{\text{NH-H}}$ = 5.4 Hz, $^3J_{\text{CH-H}}$ = 4.6 Hz), 2.56 (dt, 2H, SCH_2CH_2, $^3J_{\text{H-H}}$ = 4.6 Hz), 2.32 (t, 1H, SH, $^3J_{\text{H-H}}$ = 5.3 Hz). ^{13}C NMR ($CDCl_3$): δ = 156.4, 148.2, 129.2, 123.7, 120.8., 43.1, 25.2.

Synthesis of [(dppp)Pd(S(CH$_2$)$_2$NHC(=O)NHC$_6$H$_5$)]$_2$[TfO]$_2$ (4). [Pd(dppp)Cl$_2$] (0.118 g, 0.2 mmol) and AgSO$_3$CF$_3$ (0.103 g, 0.4 mmol) were dissolved in dry THF (10 ml) under a dinitrogen atmosphere and in the absence of light. The reaction mixture was stirred overnight and the solid AgCl formed was filtered off. The resulting filtrate containing [Pd(dppp)][CF$_3$SO$_3$]$_2$ was added to a freshly prepared mixture of HS(CH$_2$)$_2$NHC(=O)NHC$_6$H$_5$ (0.039 g, 0.2 mmol) and NaO^{t}Bu (0.019 g, 0.2 mmol) in dry THF (10 ml). The reaction mixture was stirred for 3 h changing color from light yellow to orange. After this time it was filtered under dinitrogen to eliminate traces of palladium metal formed during the reaction. The filtrate was concentrated under reduced pressure down to a half its volume (ca. 10 ml). Diethyl ether was added to the concentrated solution and the final product precipitated out of solution. The solid was filtered, washed with hexane (10 ml), and dried under reduced pressure. Yield: 97% (0.167 g). Anal. Found: C, 51.36; H, 4.19; N, 3.14. Calcd. for C$_{74}$H$_{74}$F$_6$N$_4$O$_8$P$_4$Pd$_2$S$_4$: C, 51.48; H, 4.32; N, 3.25. IR (KBr) ν = 3363 (N-H), 3054 (aromatic C-H), 2925 (aliphatic C-H), 1699 (C=O). FAB(+)-MS (m/z): 1578 (50%) [(Pd(dppp)SR)$_2$(CF$_3$SO$_3$)]$^+$. ^{31}P NMR (CDCl$_3$): δ = 11.0 (s).^{1}H NMR (CDCl$_3$): δ = 1.99 (m, 4H, PCH$_2$C*H*$_2$), 2.54 (m, 4H, SCH$_2$), 2.92 (m, 8H, PCH$_2$), 5.97 (m, 2H, S(CH$_2$)$_2$N*H*), 6.97 (t, 2H, ArH, $^3J_{H\text{-}H}$ = 7.2 Hz), 7.22 – 7.55 (several signals, 50H, ArH), 8.34 (m, 2H, N*H*-Ph).

Synthesis of Na{[(dppp)Pd(S(CH$_2$)$_2$NHC(=O)NHC$_6$H$_5$)]$_2$[TfO]$_3$} (5). [(dppp)PdCl$_2$] (0.118 g, 0.2 mmol) and AgSO$_3$CF$_3$ (0.103 g, 0.4 mmol) were suspended in dry CH$_2$Cl$_2$ (10 ml) under N$_2$ and in the absence of light. The reaction mixture was stirred overnight and the solid formed (AgCl) was filtered off. The formation of intermediate [(dppp)Pd][CF$_3$SO$_3$]$_2$ was confirmed by ^{31}P-NMR spectroscopy (singlet at 17.9 ppm in $CDCl_3$). The resulting filtrate was added to a freshly made mixture of product $HS(CH_2)_2NHC(=O)NHC_6H_5$ (0.049 g, 0.2 mmol) and $NaCO(CH_3)_3$ (0.019 g, 0.2 mmol) in dry CH_2Cl_2 (10 ml). Stirring was kept for three further hours. The reaction mixture was filtered to eliminate palladium metal and the filtrate was concentrated at reduced pressure down to a half (10 ml). Crystals suitable for X-ray analysis were obtained by crystallisation from a bi-layer of CH_2Cl_2 and hexane (20 ml). Yield: 36% (0.068 g). Anal Found: C, 47.78; H, 4.04; N, 2.89. Calcd. for $C_{75}H_{74}F_9N_4NaO_{11}P_4Pd_2S_2$: C, 47.45; H, 3.93; N, 2.95. IR (KBr) ν = 3345 (N-H), 3056 (aromatic C-H), 2924 (aliphatic C-H), 1666 (C=O), 1552 (CF_3SO_3). MS (FAB$^+$; m/z (relative intensity)): 1898 (4%) [M^+], 1749 (6%) [$(Pd(dppp)(S(CH_2)_2NH(CO)NHC_6H_5)_2(CF_3SO_3)_2Na^+$], 1578 (50%) [$(Pd(dppp)S(CH_2)_2NH(CO)NHC_6H_5)_2(CF_3SO_3)^+$]. ^{31}P-NMR (109.18 MHz, $CDCl_3$): δ = 9.0. ^{1}H-NMR (400.13 MHz, Acetone-d$_6$): δ = 1.29 (s, 4H, PCH_2CH_2), 2.10 (m, 4H, SCH_2), 2.21 (m, 4H, SCH_2CH_2), 3.13 (broad s, 8H, PCH_2), 5.79 (t, 2H, $S(CH_2)_2NH$, $^3J_{H-H}$ = 6 Hz), 6.95 (t, 2H, ArH, $^3J_{H-H}$ = 7.4 Hz), 7.26 (t, 4H, ArH, $^3J_{H-H}$ = 7.8 Hz), 7.47 – 7.65 (several signals, 44H, ArH), 8.07 (s, 2H, N*H*-Ph).

Titrations Experiments and Calculation of Association Constants

A typical anion titration was carried out in the following way: A host stock solution is done by dissolving the metal complex **4** (2.1 mg, 1.3 μmol) in dmso-d$_6$. The guest stock solution (i.e. the corresponding anion; in this case bromide) was prepared by dissolving Bu_4NBr (5.2 mg, 0.016 mmol) in 1.5 ml of the previous stock solution of **4**. An initial aliquot (0.5 ml) of the host stock solution was placed into a NMR tube and its ^{1}H NMR spectrum was determined. Additions of increasing volumes of the guest stock solution were carried out, with a micro syringe into the NMR tube, to reach, at the end, c.a. 13 equivalents. The ^{1}H NMR spectra of all the samples were measured and the changes in the chemical shifts of the urea and aromatic protons recorded. To confirm that throughout the experiment the metalla-host did not decompose, the ^{31}P NMR of the solution was measured at the beginning and at the end of the titration. The titration data obtained using ^{1}H-NMR spectroscopy were analyzed by fitting to a simple 1:1 binding isotherm using a nonlinear curve fitting program (SPECFIT/32).[3] From this analysis the association constants (see Table 1 in manuscript) were calculated.

X-Ray Structures

Fig. S1 The molecular structure of the complex cation present in the crystals of **4**.

Fig. S2 The molecular structure of the complex cation present in the crystals of **4** (10% probability ellipsoids).

Fig. S3 The molecular structure of the complex cation in the structure of **4** showing the disorder of the encapsulated triflate anion.

Fig. S4 The molecular structure of the complex cation present in the crystals of **5**.

Fig. S5 The molecular structure of the complex cation present in the crystals of **5** (30% probability ellipsoids).

Fig. S6 The molecular structure of **5** showing the disorder of the triflate anions.

The included water molecule in **5** is disordered over at least three separate sites. One of these is not that far away (*ca.* 2.65 Å) from a chlorine of one of the included dichloromethane molecules that has not been split. However, this dcm does show evidence of disorder that has been dealt with by allowing the thermal ellipsoids to expand, and thus this apparent short separation is not considered to be real and is merely an unfortunate consequence of the disorder.

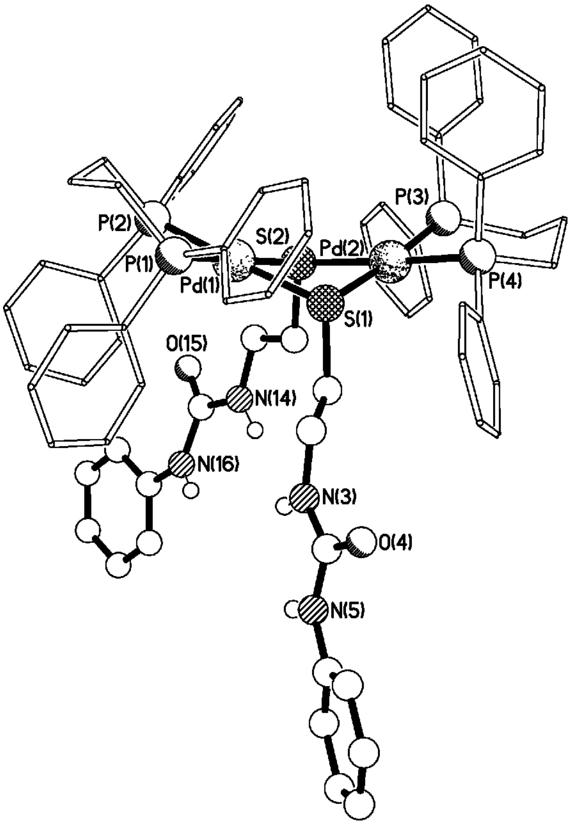

Fig. S1

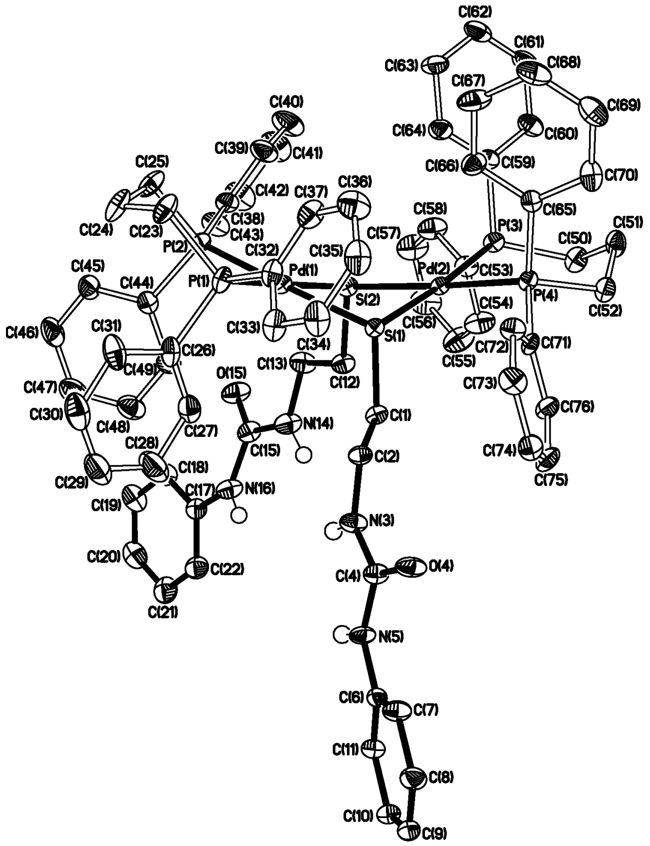
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Fig. S2

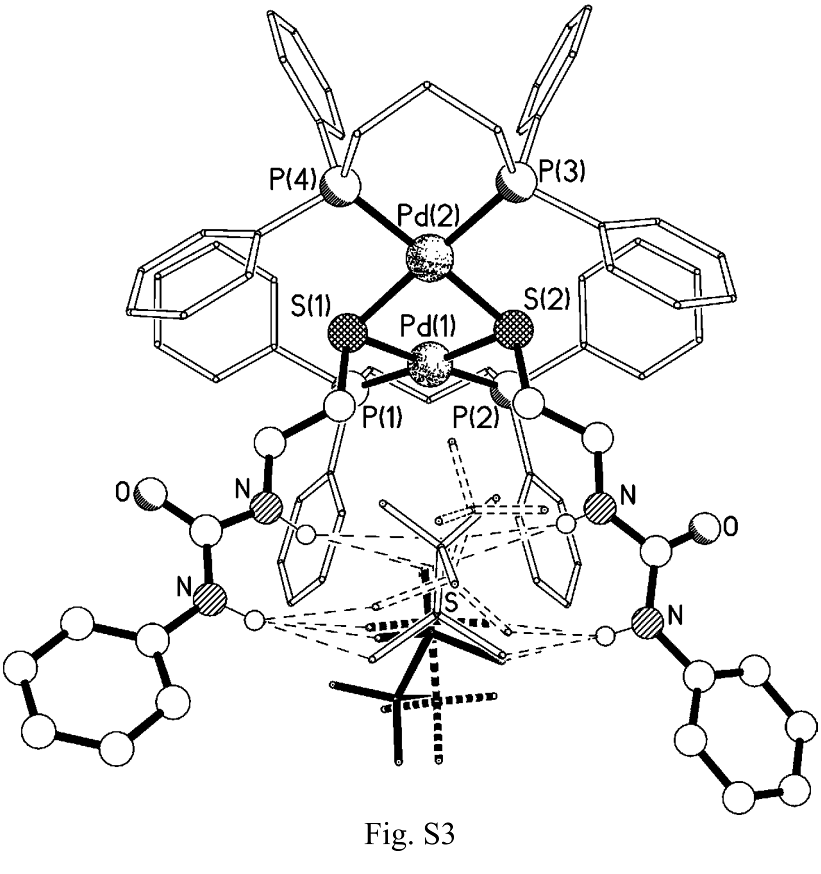
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Fig. S3

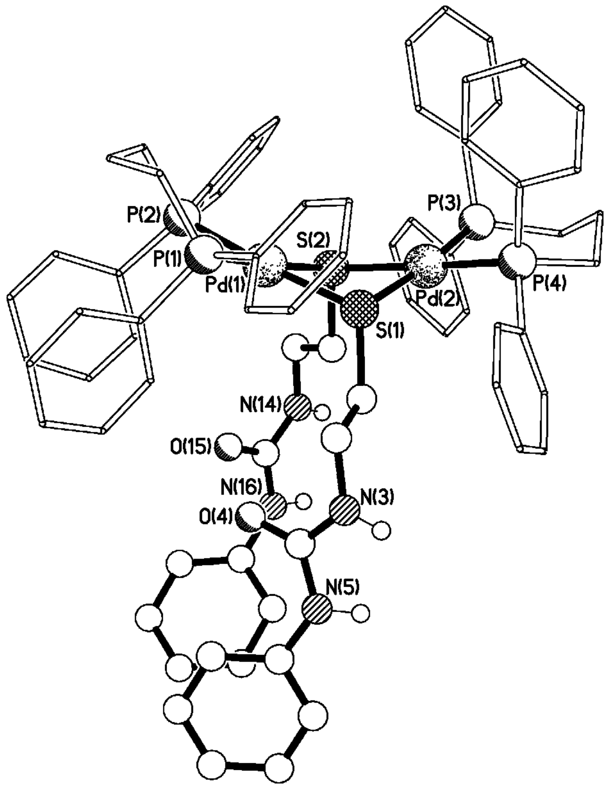
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Fig. S4

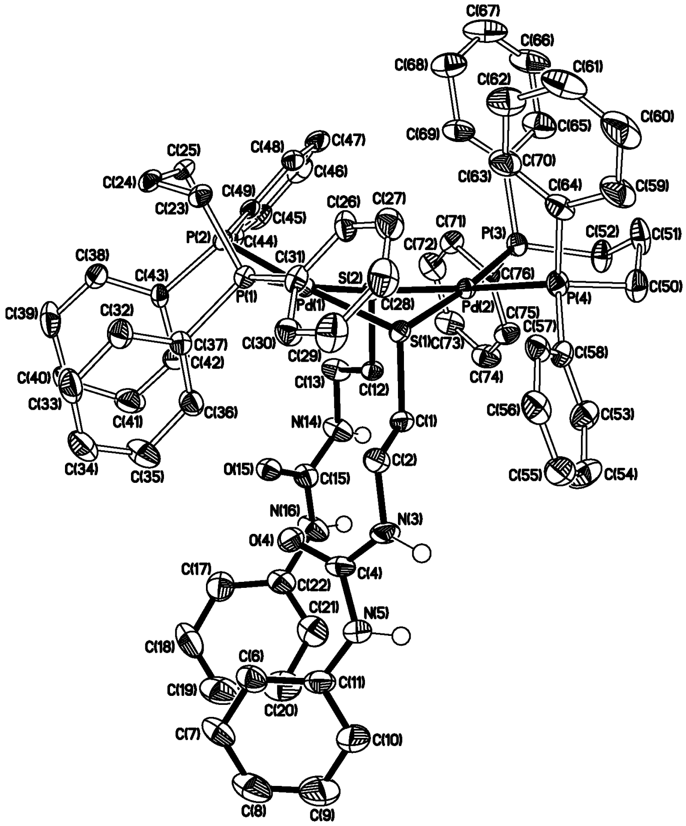
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Fig. S5

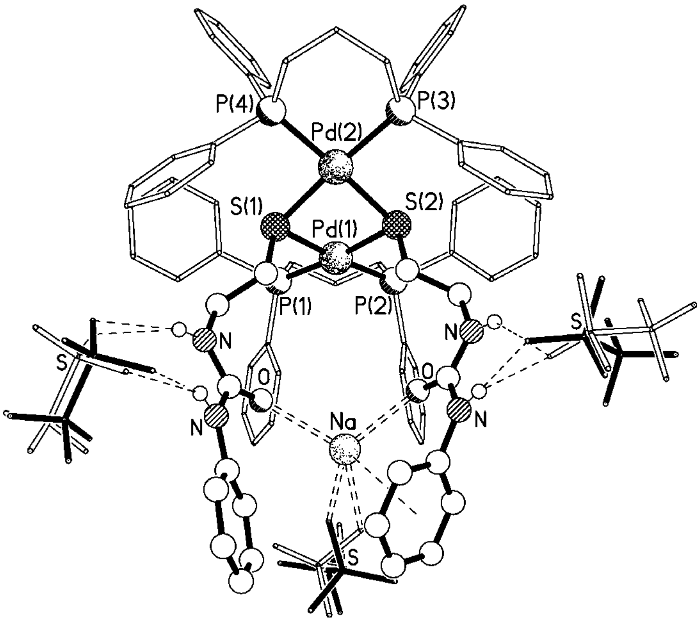

Fig. S6

References

1 W. L. Steffen, G. J. Palenik, *Inorg. Chem.*, **1976**, 15 (10), 2432-2439.

2 S. Fallis, G. K. Anderson, N. P. Rath, *Organometallics*, **1991**, 10 (9), 3180-3184.

3 R. A. Binstead, A. D. Zuberbühler, B. Jung, *Spectrum Software Associate,* Version 3.0.36, **2004**.