Isolation of an [SNS]Pd(II) pincer with a water ladder and its Suzuki coupling activity in water†

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Received (in Cambridge, UK) 5th February 2008, Accepted 26th March 2008
First published as an Advance Article on the web 30th April 2008
DOI: 10.1039/b802043d

A water-compatible Pd(II) pincer with a hybrid [SNS]-donor set, [L^1PdCl]Cl·2H_2O [L^1 = bis-(2-(*i*-butylsulfanyl)-ethyl)-amine] has been isolated and crystallographically characterized; its solid lattice at 223 K contains a ladder-like water polymer of tetramers and extensive H-bonding exists among the cation, anion and water cluster, and this water-soluble complex is active in Suzuki–Miyaura coupling of phenylboronic acid and selected aryl bromides in water at 75 °C.

The chemistry of water-based palladium-catalysed C–C bond formation reactions is a subject of topical interest.[1] One of the major challenges is the design of hydrophilic Pd(II) species of high catalytic activity with good chemical, thermal and aquatic stability. The works of Casalnuovo,[2] Nájera,[3] Miyaura[4] *etc.* are examples of such. Sajiki *et al.*[5] developed a ligand-free heterogeneous Pd/C Suzuki catalyst. Ma and Xiao[6] used palladium on modified mesoporous silica support. A chromatography-free approach was also reported by Ley *et al.*[7] Catalysts that are more resistive to oxidation have also been developed by Milstein *et al.* who used a PCP-type tridentate ligand system for Heck-type vinylation of aryl halides.[8] Other hybrid ligand sets such as [NC], [SCS] and [NCN] donors are accordingly appealing.[9] We have also been exploring a range of catalysts systems using, for example, metallomacrocycles,[10] unsaturated species,[11] hemilabile complexes,[12] multidentate hybrid-ligands,[13] N,S-heterocyclic carbenes,[14] nitrogen-rich heterocycles,[15] [PCP] pincers[16] *etc.* Each of these systems has its unique features and advantages. Our next target is to develop single-molecular dual-character catalysts that may inherit different traits and hence benefit across different catalyst systems. In this communication, we highlight such a possibility by the isolation of a water-compatible and thermally stable Pd(II) pincer that is supported by a hybrid [SNS] ligand, *viz.* [L^1PdCl]Cl·2H_2O (**1**) [L^1 = bis-(2-(*i*-butylsulfanyl)-ethyl)-amine], as well as its catalytic activity towards Suzuki–Miyaura coupling in water. In its solid-state, this complex shows an unusual "ladder-like" polymeric arrangement of the hydrate. Such low-dimensional water/ice is the structural intermediate of water clusters and bulk water.[17] It has important physical properties that are closely associated with those of the latter.[18]

Compound **1** was prepared from the reaction of $K_2[PdCl_4]$ with L^1 [L^1 = bis-(2-(*i*-butylsulfanyl)-ethyl)-amine] in an H_2O/EtOH mixture.‡ X-ray single-crystal structure analysis§ at 223 K revealed a cationic mononuclear Pd(II) pincer complex supported by a tridentate [SNS] chelating ligand (Fig. 1a). A terminal chloride completes the square planar coordination core. Each asymmetric unit comprises two lattice water molecules and an uncoordinated Cl^- ion. Its solid lattice shows that the cationic fragments are stacked upon each other to form a supramolecular network (Pd···Pd 5.364 Å) supported by van der Waals forces between Pd and the skeletal methylene proton of the ligand [C1–H···Pd1 3.87 & C7–H···Pd1 3.90 Å]. Interactions between chloride ion and the methylene [C3–H···Cl1 3.81 and C9–H···Cl1 3.78 Å] and amine [N1–H···Cl2 3.14 Å] protons are also evident (Fig. 1c).

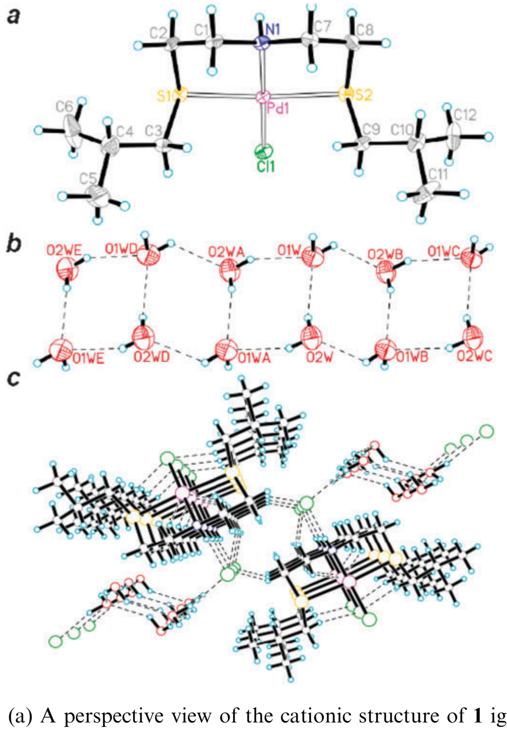

Fig. 1 (a) A perspective view of the cationic structure of **1** ignoring the anion and water solvate (thermal ellipsoids at 30% level). (Pd: purple; S: yellow; N: dark blue; Cl: green; O: red; H: sky blue). (Pd–S 2.300(1) and 2.301(1) Å; Pd–N 2.016(4) Å; Pd–Cl 2.293(1) Å); Pd(1) deviated 0.0064 Å from the mean-square plane of the donor ligands (S1, S2, N1, Cl1). (b) The H-bonding interactions in a zigzag water-ladder structure of **1** at 223 K. (Symmetry codes: A, $1 - x, 1 - y, 1 - z$; B, $2 - x, 1 - y, 1 - z$; C, $1 + x, y, z$; D, $x - 1, y, z$; E, $-x, 1 - y, 1 - z$.) (c) A lattice view along the *a* direction of the supramolecular network showing H-bonding among cation, anion and the water cluster.

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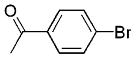
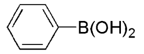
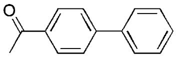
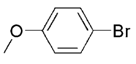
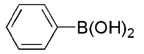
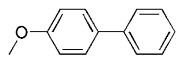
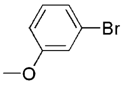
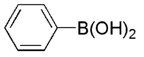
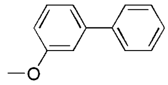
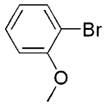
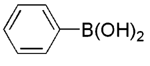
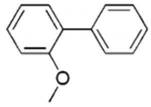
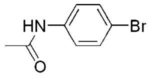
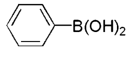
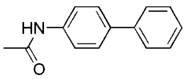
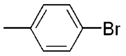
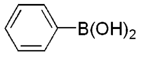
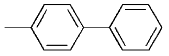
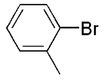
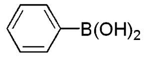
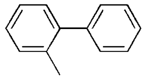
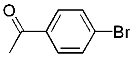
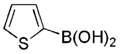
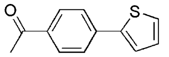
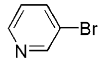
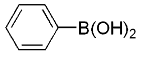
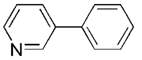
† Electronic supplementary information (ESI) available: Crystal data for **1** and **2**. CCDC reference numbers 676819 and 676820. Materials and physical measurements, Table S1, and Fig. S1 and S2. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/b802043d

Table 1 Suzuki–Miyaura coupling of arylbromide with arylboronic acid[a]

$$\mathrm{Ar^1-Br+Ar^2-B(OH)_2}\xrightarrow[\mathrm{Na_2CO_3,H_2O,75\,^\circ C,6\,h}]{\mathrm{cat-1(2\,mol\%)}}\mathrm{Ar^1-Ar^2}$$

Entry	Ar^1–Br	Ar^2–$B(OH)_2$	Product	Yield[b] (%)
1				100
2				68
3				62
4				45
5				61
6				55
7				43
8				36
9				38

[a] Conditions: 0.5 mmol Ar^1–Br, 0.6 mmol Ar^2–$B(OH)_2$, 1 mmol of Na_2CO_3, and 0.01 mmol of cat-**1** (2 mol%) in 5 mL H_2O at 75 °C for 6 h. [b] GC-MS yield.

A notable feature of the pincer lattice at 223 K is the presence of a step-like water polymer propagated by H-bonds in a zig-zag manner (Fig. 1b). If O1W···O2W···O1WA···O2WA is viewed as a tetramer (O1W···O2W 2.82 Å; O1W···O2WA 2.90 Å), this water cluster can be treated as a polymer of interconnecting tetramers (O1W···O2WB 2.94 Å). The average O···O separation (2.89 Å) is slightly longer than those in liquid water tetramer (2.78 Å),[19a] liquid water (2.854 Å),[19b,c] or ice (2.77–2.84 Å).[19d] This could be attributed to the multitude of H-bonds within the polymer and with the chloride ions (O1W–H···Cl2 3.11 Å). The dihedral angle between the two mean tetrameric planes (O1W···O2W··· O1WA···O2WA and O1W···O2W···O1WB···O2WB) is 45.7°, whereas the torsion angle of O2WA···O1W···O2WB···O1WC is 0°. We are not aware of similar step-alignment of polymeric tetra-aqua structures in other hydrate systems. The aqua polymers are linked to the supramolecular layers of the pincer through H-bonding with chloride ions which in turn are H-bonded with the amine and methylene protons (Fig. 1c). These collectively give a 3-D supramolecular framework stabilized extensively by H-bonds across all three key entities of pincer cation, uncoordinated Cl^- ions and lattice hydrate (Table S1 and Fig. S1 in ESI†). Thermal gravimetric analysis (Fig. S2 in ESI†) of a fresh sample showed a weight-loss at 40–85 °C of 7.5%, which corresponds to complete dehydration (calculated 7.9%). The complex is stable up to ~160 °C, beyond which decomposition occurs.

The hydrophilic nature of **1** enables it to dissolve in water to promote Suzuki–Miyaura coupling reactions of selected aryl and heterocyclic bromides and phenylboronic (and heteroaryl) acid at 75 °C. Some selected data are given in Table 1. For 4-bromoacetophenone (entry 1), it gives near-quantitative yields at catalyst loadings of 2.0–0.4 mol% Pd (Fig. 2). The yield drops to 33% when the catalyst loading reaches the limit of 0.1 mol%. Towards unactivated 4-bromoanisole, **1** (2 mol%) gives 68% yield of 4-anisobiphenyl (entry 2). The yields towards unactivated bromides are only moderate (36–68%, entries 2–9).

Similar experiments using bis-(2-(benzylsulfanyl)-ethyl)-amine (L^2) as the ligand also yielded an analogous pincer $[L^2PdCl]Cl$ (**2**) (Fig. 3). The multidentate pincer effect overcomes the weak basicity of the thioether functions, to the extent that the metal prefers a pincer with two fused 5-membered-rings to the alternative of a chelating $[PdCl_2(SNS)]$ with a pendant thioether. There is no water cluster in **2**. Instead, the Cl^- counter-anion is weakly linked to the amine, methylene and benzyl protons. Complex **2** is not active towards activated 4-bromoacetophenone acid at 2 mol% under similar conditions. This significant catalytic difference between **1** and **2** is surprising. Current experiments are directed at the tuning of the electronic character of the donor substituents and the hydrophilic character of the complex.

This work suggests that conventional organic-based pincer complexes could be introduced to the field of water-based catalysis. This is achieved by designing a supramolecular framework that can incorporate water clusters or polymers. Key to this strategy is the stacking of structurally compatible cations and their electrostatic interaction with hydrophilic anion. The latter serves as additional hydrophilic centers to attract hydrate through H-bonding. The columnar arrangement also creates

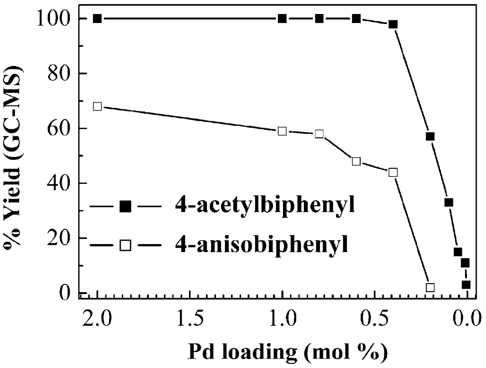


Fig. 2 Yield of 4-acetylbiphenyl (■) and 4-anisobiphenyl (□) at 75 °C for 6 h in water as a function of catalyst (**1**) load.

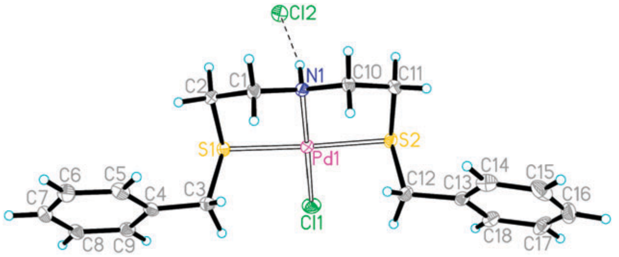


Fig. 3 A perspective view of the structure of **2** (ellipsoids at 30% level). (Pd–S 2.2920(5) and 2.2929(5) Å; Pd–N 2.030(2) Å; Pd–Cl 2.3075(6) Å); Pd(1) deviated 0.0185 Å from the mean-square plane of the donors (S1, S2, N1, Cl1). H-bonding interaction of N1–H1N···Cl2 is observed.

room for the formation of a water channel in the form of water steps. The anion lends additional stability to the 3-D structure by connecting the hydrate to the cation. Collectively, they improve the water compatibility of the pincer and mark a significant step towards the construction of water-rich metallic materials. It also expands the scope of aqueous catalysis and points a way forward for water transport in inherently non-aqueous systems.

This work was supported by the Agency for Science, Technology & Research (Singapore) and the National University of Singapore (143-000-277-305). We are grateful to Dr L. L. Koh and Ms G. K. Tan for assistance in the X-ray diffraction experiments and structural refinement.

Notes and references

‡ Preparation: the SNS ligands L^1 and L^2 were prepared by literature methods.[20] Complexes **1** and **2** were prepared by a common procedure as follows: an aqueous solution of $K_2[PdCl_4]$ (326 mg, 1 mmol) was mixed with an ethanol solution of L^1 (249 mg, 1 mmol) or L^2 (318 mg, 1 mmol). Upon standing for ~2 weeks, yellowish prismatic crystals suitable for X-ray diffraction experiments were collected. For **1**, yield: 260 mg (56%). ^{1}H-NMR (300 MHz, $CDCl_3$, 25 °C): δ = 1.05–1.08 (m, 12H, CH_3), 1.82 (s, 4H, H_2O), 1.95–2.13 (m, 2H, $CH_2C\mathit{H}(CH_3)_2$), 2.81–3.49 (m, 12H, CH_2). ^{13}C-NMR (75.47 MHz, $CDCl_3$, 25 °C): δ = 21.1 (s, CH_3), 22.0 (s, CH_3), 27.8 (s, $CH_2\mathit{C}H(CH_3)_2$), 39.5 (s, $CH_2\mathit{C}H_2S$), 49.7 (s, $S\mathit{C}H_2CH$), 54.9 (s, $NH\mathit{C}H_2CH_2$). Elemental analysis calcd $C_{12}H_{31}C_{12}NO_2PdS_2$ (462.8): C, 31.14; H, 6.75; N, 3.03. Found: C, 31.53; H, 6.57; N, 3.20%. Selected IR data (cm^{-1}, KBr): 3493 v, 3441 v, 3000 m, 2963 v, 2846 v, 1621 m, 1465 m, 1421 m, 1382 m, 1259 m, 496 m. For **2**, yield: 350 mg (70%). ^{1}H-NMR (300 MHz, $(CD_3)_2SO$, 25 °C): δ = 2.81–3.13 (m, 8H, $NHC\mathit{H}_2C\mathit{H}_2S$), 4.44–4.58 (m, 4H, $SC\mathit{H}_2Ph$), 7.40–7.56 (m, 10H, Phenyl H). ^{13}C-NMR (75.47 MHz, $(CD_3)_2SO$, 25 °C): δ = 36.1 (s, $S\mathit{C}H_2Ph$), 54.4 (s, $NH\mathit{C}H_2\mathit{C}H_2S$), 128.6, 129.2, 129.9, 133.7 (s, Ar-C). Elemental analysis calcd $C_{18}H_{23}C_{12}NPdS_2$ (494.79): C, 43.69; H, 4.68; N, 2.83. Found: C, 43.49; H, 4.61; N, 2.82%. Selected IR data (cm^{-1}, KBr): 3448 b, 2973 m, 2919 m, 2816 m, 2735 v, 1492 m, 1455 m, 1420 m, 1240 m, 1073 m, 1024 m, 1004 m, 799 m, 770 v, 700 v, 636 m. General procedure for Suzuki–Miyaura coupling reactions: a 15 mL vial was charged with activated or deactivated aromatic bromide (0.5 mmol), aryl boronic acid (0.6 mmol), Na_2CO_3 (1 mmol), SNS–Pd catalyst (**1**), and H_2O (5 mL), the mixture was stirred at 75 °C in air for 6 h. The products were assayed by GC-MS.

§ Crystal data for **1**: formula $C_{12}H_{31}Cl_2NO_2PdS_2$, yellow crystal, triclinic space group $P\bar{1}$; a = 5.3641(7), b = 13.405(2), c = 15.300(2) Å; α = 67.357(2), β = 84.856(2), γ = 80.298(2)°; V = 1000.5(2) Å^3; Z = 2; crystal size: 0.40 × 0.10 × 0.06 mm^3; GOF = 1.087; reflections collected: 8989; independent reflections: 3524 [R_{int} = 0.0333]; R_1 = 0.0446; wR_2 = 0.1161. Crystal data for **2**: formula $C_{18}H_{23}Cl_2NPdS_2$, yellow crystals, monoclinic space group $P2_1/n$; a = 12.3815(6), b = 5.6441(3), c = 28.793(2) Å; β = 99.376(1)°; V = 1985.2(2) Å^3; Z = 4; crystal size: 0.70 × 0.24 × 0.10 mm^3; GOF = 1.027; reflections collected: 13376; independent reflections: 4540 [R_{int} = 0.0270]; R_1 = 0.0249; wR_2 = 0.0621. Data **1** and **2** were collected on a Bruker AXS CCD diffractometer with Mo-K$_\alpha$ radiation (λ = 0.71073 Å) at 223 K. The structures were solved by direct methods and refined by a full matrix least squares technique based on F^2 using SHELXL 97 program.[21] The hydrogen atoms on carbon were constrained. For complex **1**, H atoms H1N, H1W, H2W, H3W, H4W were located from difference map, the positions were refined with constraints DFIX 0.90(2) for N–H, DFIX 0.85(2) for O–H, and DFIX 1.20(2) for H···H of water, with thermal parameter at −1.2000 of the relevant N or O. CCDC No.: 676819 (**1**) and 676820 (**2**).

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