A di-palladium urea complex as a molecular receptor for anions†

Jorge A. Tovilla,[ab] Ramón Vilar*[ac] and Andrew J. P. White[b]

A new di-nuclear palladium complex containing thiol-urea ligands has been prepared, structurally characterized and its interaction with anionic species studied in solution.
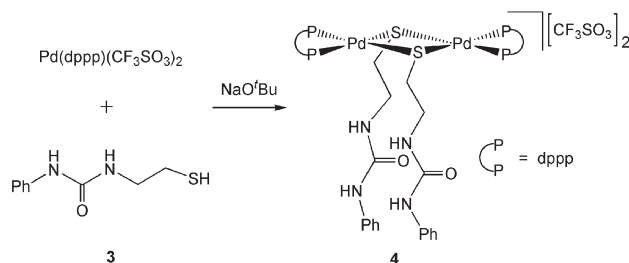
The synthesis of molecular receptors that can selectively recognize specific guests is a topic of current interest due to the important applications that these species can have in the development of sensors, probes and selective catalysts.[1] Although initially more attention was paid to receptors that could bind cations and neutral species, over the past few years an increasing number of molecular hosts for the selective recognition of anionic guests have been developed.[2,3] A particularly appealing approach for the design of receptors for anions is to combine the structural and functional properties of metal centres with the recognition capabilities of hydrogen bonding groups.[4–8] Not only do metal centres often provide a positive charge to the receptor (increasing the electrostatic attraction between the host and the anionic guest) but they also act as structural motifs to organize the hydrogen bonding moieties for optimal binding. Furthermore, the metal can confer to the receptor useful optical, electrochemical or catalytic properties.

Herein we report a new di-palladium complex with urea-containing ligands that binds several anions in dmso solutions. The design of the metalla-receptor is based on two square-planar palladium centres linked by bridging thiolate ligands that contain urea groups as hydrogen bonding units (see Scheme 1).

The urea-containing ligand $HSCH_2CH_2NHC(=O)NHPh$ was prepared in three steps. The reaction between di-cystamine hydrochloride—in which the thiol is protected as disulfide—and phenylisocyanate (PhNCO) was first carried out to yield the urea disulfide $[-SCH_2CH_2NHC(=O)NHPh]_2$ (1). This species was then reduced with PPh_3 and protonated with HCl to yield the corresponding thiol. The thiol was purified by forming the insoluble lead thiolate $Pb[SCH_2CH_2NHC(=O)NHPh]_2$ (2) which was easily isolated by precipitation. Upon treating 2 with HCl the thiol-urea ligand $HSCH_2CH_2NHC(=O)NHPh$ (3) was isolated as an analytically pure compound.

The metalla-receptor $[Pd(dppp)\{\mu-SCH_2CH_2NHC(=O)-NHPh\}]_2[CF_3SO_3]_2$ (4) was obtained from the reaction between $Pd(dppp)(CF_3SO_3)_2$ and one equivalent of the thiol in the presence of NaO^tBu. Complex 4 was crystallized out of this solution and characterized by spectroscopic, analytical and structural methods (see the ESI for experimental details of all the compounds prepared in this work†). The $^{31}P\{^1H\}$ NMR spectra of 4 indicate that there is only one type of phosphorus in the complex since only a singlet was observed (at 11.0 ppm). The FAB(+) mass spectrum of this compound showed strong peaks corresponding to $[4–CF_3SO_3]^+$. In order to establish the exact conformation of the di-palladium complex and gain some insight into the host–anion interactions, the single crystal X-ray structure of 4 was determined (see Fig. 1).‡
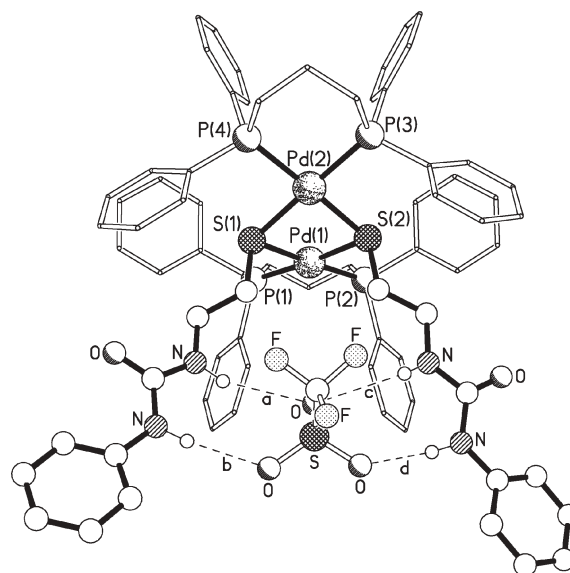

Scheme 1

Fig. 1 The molecular structure of the complex cation in the structure of 4 showing the encapsulation of one of the disordered triflate anions (see text) by N–H···O hydrogen bonding interactions. The hydrogen bonding geometries, [N···O], [H···O] (Å), [N–H···O] (°) are (a) 3.38(3), 2.53, 159; (b) 3.16(2), 2.27, 173; (c) 3.30(3), 2.59, 136; (d) 3.23(3), 2.35, 165.

[a]Institute of Chemical Research of Catalonia (ICIQ), Avgda. Països Catalans 16, 43007 Tarragona, Spain. E-mail: rvilar@iciq.es; Fax: +34 977 920 228; Tel: +34 977 920 212
[b]Department of Chemistry, Imperial College London, London, UK SW7 2AZ
[c]Institution of Advanced Studies and Research of Catalonia (ICREA), Spain
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As expected, the dicationic complex has both of the thiolate ligands on the same side of the central Pd_2S_2 ring (see Fig. 1 below and Fig. S1 in the supplementary data†). This ring is folded about the S···S vector, the two square-planar palladium coordination planes being inclined by *ca.* 35°. Of most interest is the encapsulation of one of the triflate anions between two thiolate ligand arms by virtue of N–H···O hydrogen bonding from the urea groups (see Fig. 1).[9]

Interestingly, slight changes in the purification and crystallization techniques employed to obtain crystalline samples of **4** led to the formation of a different compound, namely the di-nuclear complex $Na\{[(dppp)Pd(\mu\text{-}SCH_2CH_2NHC(=O)NHC_6H_5)]_2[TfO]_3\}$ (**5**) in which an Na^+ cation (coming from the NaO^tBu used to deprotonate the thiol) and an extra triflate anion are included in the structure. This was established by an X-ray crystallographic study (see Fig. 2).§ As was seen in the structure of **4**, in **5** the thiolate ligands are again oriented on the same side of the Pd_2S_2 ring (Fig. S4), and the two palladium coordination planes are inclined similarly (here by *ca.* 37° *cf.* 35° in **4**). The presence of a sodium cation, however, leads to a very different orientation of the urea group within each thiolate ligand (Fig. 2). In the structure of **4** the N–H groups were oriented inwards to allow the formation of N–H···O hydrogen bonds to one of the triflate anions,[10] whereas here in **5** it is the carbonyl oxygens that point inwards to encapsulate the sodium cation. The binding to the sodium cation is supplemented by an Na···π contact at *ca.* 3.26 Å to the terminal phenyl ring of one of the thiolate arms (the Na···centroid vector is inclined by *ca.* 73° to the ring plane). It is thus clear that these thiolate-urea ligands give the complex the versatility to act as a host for both cationic and anionic guests.

To evaluate the anion binding abilities of the di-metallic complex **4** in solution, titrations of the hosts with several anionic species in deuterated dmso were carried out. The host–guest
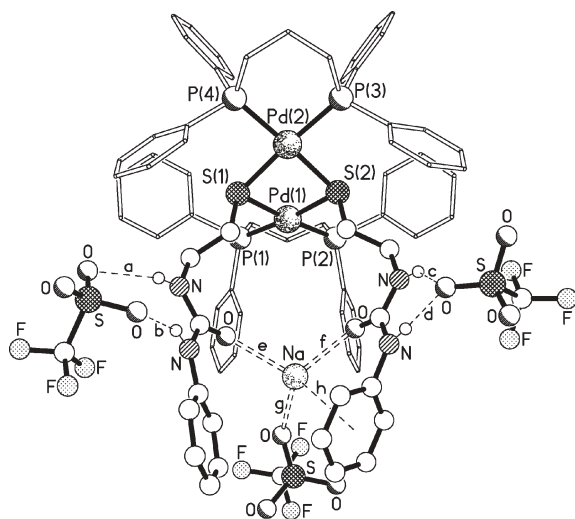

Fig. 2 The molecular structure of **5** showing the Na···O interactions. Two of the three triflate anions are linked to the periphery of the thiolate arms by N–H···O hydrogen bonds, whilst the third binds to the sodium cation (all three triflate anions are disordered, see text). The H-bonding geometries, [N···O], [H···O] (Å), [N–H···O] (°) are (a) 3.365(18), 2.50, 165; (b) 2.785(14), 1.93, 158; (c) 3.086(12), 2.30, 146; (d) 2.901(12), 2.01, 172. The Na···O contact separations (Å) are (e) 2.511(8); (f) 2.412(8); (g) 2.509(11).

Table 1 Association constants (log K_a)[a] in dmso solution

Anion	4
PF_6^-	~0
SO_4^-	2.4 ($\pm$0.05)[b]
Cl^-	2.9 ($\pm$0.05)
Br^-	3.3 ($\pm$0.09)
$P(=O)(OH)(OPh)O^-$	3.4 ($\pm$0.03)
$H_2PO_4^-$	3.5 ($\pm$0.08)

[a] Determination by ^{1}H NMR spectroscopy monitoring the changes in the chemical shift of the urea protons. [b] Standard deviation corresponding to the fit of the experimental data to the calculated curve.

interactions were investigated by ^{1}H NMR spectroscopy. The changes in chemical shift of the urea protons (both from the NH's and the phenyl group) of the complex were recorded upon adding increasing amounts of the different anions. As can be seen in Table 1, **4** indeed acts as a good molecular receptor for anionic species. Although this complex is di-positively charged and hence could bind two mono-charged anions independently, with the model employed to fit the experimental titration data there is no indication of the presence of two distinct binding constants.

As discussed before, the crystal structures of **4** and **5** show that in the solid state the triflate anions hydrogen bond to the urea groups of the metalla-receptor. To establish if these interactions were retained in dmso solution, a dilution experiment of **4** and a titration of the "free" thiol-urea **3** with triflate, were carried out. Both of these experiments indicate that in dmso, there are no significant hydrogen bonding interactions between triflate and the urea groups of **3** and **4** (which is not surprising since dmso is known to interact strongly with ureas while triflate binds to them weakly).

The metalla-receptor shows a degree of selectivity towards anions such as phosphate and phosphoester. Although the discrimination between anions is not very high, there is a clear trend in the binding abilities of **4**: $PF_6^- \sim CF_3SO_3^- < SO_4^{2-} < Cl^- < Br^- \sim H_2PO_4^- \sim P(=O)(OH)(OPh)O^-$.

In conclusion, a new type of metal-containing receptor for anionic guests has been prepared and structurally characterized. Due to the presence of phenylurea groups, under certain conditions, the receptor is also able to bind simultaneously anions and cations. We are currently carrying out further studies to increase the selectivity of the receptor for phosphorylated species.

Notes and references

‡ *Crystal data for* **4**: $[C_{72}H_{74}N_4O_2P_4Pd_2S_2](CF_3SO_3)_2 \cdot C_4H_8O$, $M = 1798.40$, monoclinic, $P2_1/c$ (no. 14), $a = 14.557(3)$, $b = 23.299(3)$, $c = 26.168(3)$ Å, $\beta = 98.921(11)$ °, $V = 8768(2)$ Å^3, $Z = 4$, $D_c = 1.362$ g cm^{-3}, μ(Mo-Kα) = 0.644 mm^{-1}, $T = 293$ K, pale brown/orange blocks; 12837 independent measured reflections, F^2 refinement, $R_1 = 0.065$, w$R_2 = 0.145$, 7744 independent observed absorption-corrected reflections [$|F_o| > 4\sigma(|F_o|)$, $2\theta_{max} = 47°$], 1000 parameters. CCDC 276098. See http://dx.doi.org/10.1039/b509565d for crystallographic data in CIF or other electronic format.

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9 This triflate anion is actually highly disordered, four separate orientations having been identified in the crystal (Fig. S3). In each case however, the three oxygen atoms are in approximately the same position. Thus, the hydrogen bond geometries quoted in the figure caption (which are for the major occupancy orientation) should be regarded as indicative only.

10 Again the triflate anions are disordered (Fig. S6), two positions having been located in each case. Only the major occupancy orientations are drawn in Fig. 2 and described in the caption.