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Di-palladium Complexes with Urea-containing Ligands as Anion Receptors

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A series of di-palladium complexes with thiolato ligands containing urea groups for hydrogen bonding have been prepared. Three of these complexes have been structurally characterised by X-ray crystallography showing some interesting supramolecular interactions between the metal complexes and counter-anions. ^{31}P NMR solution studies have been carried out to gain some insight into the different conformations of the complexes in solution. To support the experimental findings, computational studies have been performed demonstrating the preference for one of the two conformers in the presence of the appropriate solvent and anion. The anion-binding properties of two of these metallo-receptors have been studied by ^{1}H NMR spectroscopy. Binding constants (in DMSO) between the receptors and specific anions (e.g., $[H_2PO_4]^-$) are in the order of 10^3.

Keywords: Di-palladium complexes; Anion receptors; Metallo-receptors; Binding constants

INTRODUCTION

The development of molecular receptors that can selectively recognise and detect anionic analytes is a topic of great current interest [1–7]. This is partly due to the important roles that anions play in biological systems (e.g., phosphorylated species) and the environment (e.g., cyanide and nitrate). An interesting approach to develop anion receptors is to combine the structural and functional properties of metal centres with the recognition capabilities of hydrogen-bonding groups [8,9]. Metal centres can act as flexible structural motifs to organise the hydrogen bonding moieties for optimal binding and also confer useful optical [10–12], electrochemical [13–15] or catalytic properties to the receptor. Over the past few years, several metallo-hosts for anions have been reported [16–20]. Among the first examples of this approach are the metallocene-based receptors reported by Beer [14,21] and the uranyl complexes reported by Reindhout in which the host–anion interactions could be detected electrochemically [22–26]. Several groups have employed luminiscent ruthenium complexes with substituted bipyridines as chemical sensors for anions [27–35]. More recently, Gale and Loeb have reported a series of platinum complexes with substituted pyridine ligands as metallo-receptors for anions [20,36,37] while Anslyn has demonstrated that copper complexes of tridentate ligands (with a C_{3v} symmetry) can selectively bind phosphates with high associations constants [38].

As part of our ongoing interest in developing metallo-receptors for anions [39–45], we have recently reported in a preliminary communication the synthesis and crystal structure of di-palladium complex **1** (see Fig. 1) [46]. This compound has been demonstrated to bind anions in DMSO solutions.

The design of the metallo-receptor is based on two square-planar palladium centres linked by bridging thiolate ligands that contain urea groups as hydrogen bonding units. In this paper, we report the synthesis of two thiol-urea ligands and the preparation of their corresponding palladium(II) dimeric complexes. The solid state structure of these compounds, their stability in solution and their anion-binding properties have also been investigated. In order to rationalise some of the experimental results,

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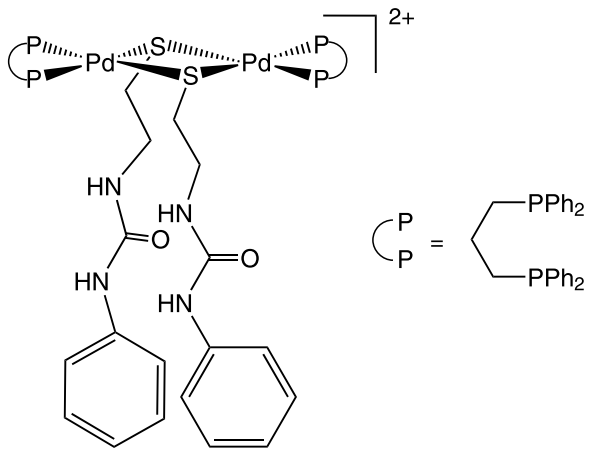


FIGURE 1 Molecular structure of the di-cationic metallo-host **1**.

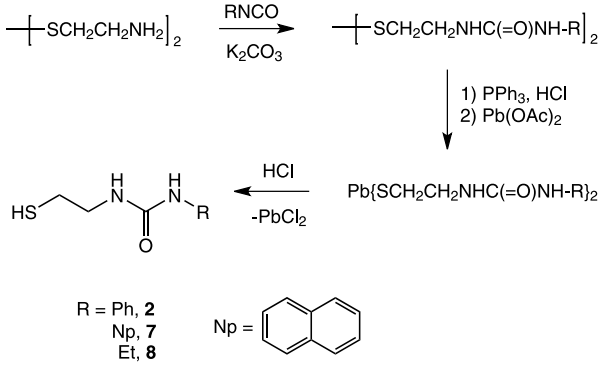
computational studies have been carried out on model compounds.

RESULTS AND DISCUSSION

Synthesis of Thiol-urea Ligands

In our preliminary communication we reported that the urea-containing thiol ligand $HS(CH_2)_2$-NH(C═O)NH—Ph (**2**) can be prepared in three steps (see Scheme 1), starting from the commercially available cystamine dihydrochloride, $H_2N(CH_2)_2$-S—S$(CH_2)_2NH_2$·2HCl. Using an analogous synthetic procedure, the thiol-urea ligands $HS(CH_2)_2$-NH(C═O)NH-R (R = CH_2CH_3, 1-$C_{10}H_7$) have been prepared.

The reaction between the disulfide diamine and the corresponding isocyanates, RNCO (R = CH_2CH_3 and 1-$C_{10}H_7$) yielded the diurea disulfide compounds [—$S(CH_2)_2NH(C═O)NH$-R]$_2$ (R = 1-$C_{10}H_7$, **3**; CH_2CH_3, **4**). These species were then reduced with PPh_3 and protonated with HCl to give the corresponding thiols which were purified by forming the corresponding lead thiolates Pb[$S(CH_2)_2NH(C═O)NH$-R]$_2$ (R = 1-$C_{10}H_7$, **5**; CH_2CH_3, **6**). These complexes are insoluble and can be easily isolated by filtration. After filtration, **5** and **6** were treated with diluted HCl to yield the corresponding pure thiol-urea ligands $HS(CH_2)_2$-NH(C═O)NH-R (R = 1-$C_{10}H_7$, **7**; CH_2CH_3, **8**).



SCHEME 1 Schematic representation of the synthesis of thiol-urea ligands **2**, **7** and **8**.

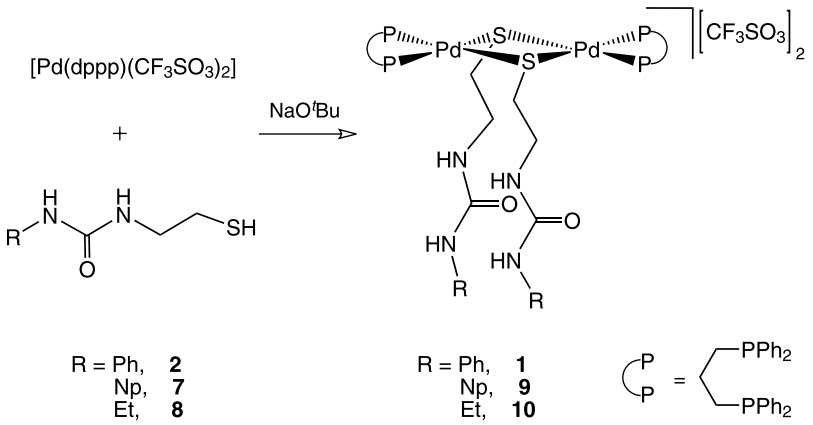
Synthesis of Palladium-based Receptors Containing Thiolato-urea Bridging Ligands

In our preliminary communication [46] we reported that [Pd(dppp){μ-$S(CH_2)_2NH(C═O)NH$—Ph}]$_2$[CF_3-SO_3]$_2$ (**1**) can be readily prepared from [Pd(dppp)(CF_3SO_3)$_2$] and one equivalent of thiol (**2**) in the presence of NaO^tBu (see Scheme 2).

In order to investigate whether a larger aromatic substituent on the thiolate-urea ligand would have an influence on the anion binding, the analogous di-palladium complex derived from the naphthyl-containing thiol **7** (see Scheme 1) was prepared. The synthesis of [Pd(dppp){μ-$S(CH_2)_2$-NH(C═O)NH—Np}]$_2$[CF_3SO_3]$_2$ (**9**) was carried out by an analogous procedure to the one used to prepare **1**. The di-palladium complex was isolated by precipitation with hexane from a THF solution and fully characterised by spectroscopic and analytical means. The $^{31}P\{^1H\}$ NMR spectrum of **9** indicated the presence of only one type of phosphorus (singlet at 11.4 ppm). The FAB(+) mass spectrum of the complex gave a peak at 1826 a.m.u. which can be assigned to $[\mathbf{9}]^+$ and, therefore, is consistent with the proposed formulation.

The structure of compound **9** was unambiguously elucidated by single crystal X-ray structural analysis (from single crystals obtained by slow diffusion of hexane into the THF reaction mixture). The asymmetric unit contains two independent molecules of **9** with different conformations. One of the molecules is represented in Fig. 2. Additionally in the elementary cell, four triflate anions, four tetrahydrofurane molecules and three positions for water molecules could be localised. The water molecules are partly disordered (hydrogen atoms were not localised) with a total occupation ratio of 1.33 oxygen atoms. The palladium and the sulfur atoms form a folded Pd_2S_2 ring with an angle of 141.8°/144.2° (molecule A/B). For molecule A the Pd-S distances are 2.3749(9), 2.3766(10), 2.3793(9) and 2.3809(10) Å and the Pd···Pd separation is 3.267(2) Å. For molecule B, Pd-S: 2.3818(10), 2.3877(11), 2.3797(11) and 2.2874(12) Å, and Pd···Pd: 3.321(2) Å.

For each independent molecule, one of the triflate anions is located close to one of the metal centers (the closest O2S···Pd1 distance is 4.58 Å) and displays hydrogen bonds to the urea groups with the following distances: O1S···N1: 2.970/2.925 Å, O1S···N2: 2.968/2.961 Å, O2S···N3A: 3.260/3.139 Å and O3S···N4A: 3.146/3.398 Å (for A and B respectively). The remaining triflate anions are



SCHEME 2 Synthetic scheme for the preparation of the di-palladium metallo-hosts **1**, **9** and **10**.

located in-between the complexes, making only some weak contacts to neighboring aromatic rings. In the crystal packing only weak intermolecular interactions can be observed.

Once the detailed formulation and structure of this compound was established, the synthesis of an analogous complex using a thiolate-urea ligand with a smaller and not aromatic substituent (i.e., an ethyl group) was investigated. An analogous reaction to the one described for the synthesis of both **1** and **9** was carried out using thiol **8** (see Scheme 2). The $^{31}P\{^1H\}$ NMR spectrum of the reaction mixture showed only one singlet at 11.1 ppm which was assigned to the formation of the thiolato-bridged di-palladium complex. A solid was isolated from the reaction mixture and characterised spectroscopically and analytically. However, instead of the expected di-palladium species $[Pd(dppp)\{\mu\text{-}S(CH_2)_2\text{-}NH(C{=}O)NH\text{-}Et\}]_2[CF_3SO_3]_2$ (**10**), the characterisation was consistent with the slightly different formulation $Na\{[Pd(dppp)\{\mu\text{-}S(CH_2)_2NH(C{=}O)NH\text{-}Et\}]_2[CF_3SO_3]_3\}$ [**10**][$NaCF_3SO_3$]. In the latter, a Na^+ cation and an extra $[CF_3SO_3]^-$ anion are associated to the di-palladium metallo-host. An analogous product was previously obtained and fully characterised (including an X-ray crystal structure) for the thiolato-urea ligand containing a phenyl substituent. As reported in our previous preliminary communication in that case it was possible to selectively obtain either **1** or [**1**][$NaCF_3SO_3$] by changing the crystallisation conditions. Consequently, the crude solid obtained from the reaction between $[Pd(dppp)(CF_3SO_3)_2]$ and the ethyl-substituted thiolate-urea ligand **8** was purified using different solvents and procedures. In spite of several attempts to selectively crystallise **10** without the extra $NaCF_3SO_3$ salt, we consistently obtained [**10**][$NaCF_3SO_3$] as revealed by elemental analyses.

To avoid this problem and also to reduce the number of steps needed to prepare the thiolate-bridged

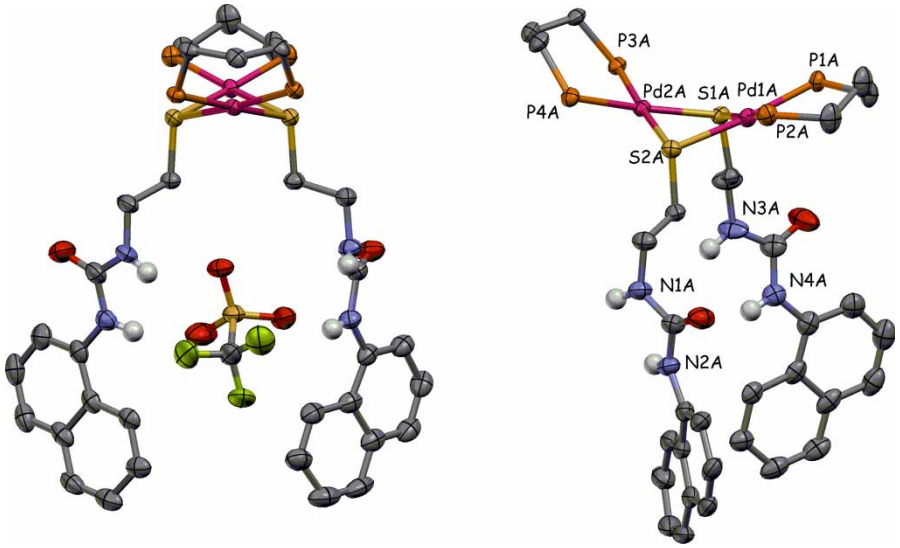


FIGURE 2 Ortep-plot (thermal ellipsoids shown at 50% probability level) of **9** in a front (showing only one triflate anion for clarity) and a side (with no triflate anions shown) view. Phenyl rings of the dppp ligands and the molecule's hydrogen atoms (except those of the urea groups) have been omitted for clarity.

di-palladium complexes, we investigated whether the direct reaction between [Pd(dppp)Cl_2] and Pb{SCH_2-$CH_2NHC(=O)NHEt\}_2$ would yield the same compound but with no $NaCF_3SO_3$ contamination (and chloride counter-anions instead of triflates). Upon mixing these two compounds and stirring for 24 h, the ^{31}P-{^1H} NMR spectrum of the reaction mixture indicated that all the starting materials had been consumed and only one phosphorous-containing product with $\delta = 11.3$ ppm had been formed. This chemical shift is very close to the values observed for **1**, **9** and **10**; therefore, it was concluded that this synthetic route was successful. A solid was isolated from the reaction mixture and fully characterised as [Pd(dppp){μ-$S(CH_2)_2NH(C=O)NH$-Et}]$_2Cl_2$ (**11**) by spectroscopic, structural and analytical means.

Single crystals of **11** were obtained by slow diffusion of hexane into aliquots of the reaction mixture. One of the crystals was analysed by X-ray crystallography allowing us to unequivocally establish the structure of this complex (see Fig. 3). The Pd_2S_2 ring (distances: Pd-S: 2.406(2)/2.374(2)/2.379(2)/2.367(3) Å and Pd···Pd: 3.314(2) Å) is folded with the planes of the bridging sulfur atoms forming an angle of 141.3°. The asymmetric unit contains one molecule of **11**, two chloride anions, three positions of water molecules and two disordered dichloromethane molecules. Both chlorides are disordered in two positions with a 50:50 occupation ratio. One of the water molecules is clearly localised between the urea groups forming a network of hydrogen bonds. The remaining positions of the water molecules have an occupation of 50%, are disordered and localised inside a channel

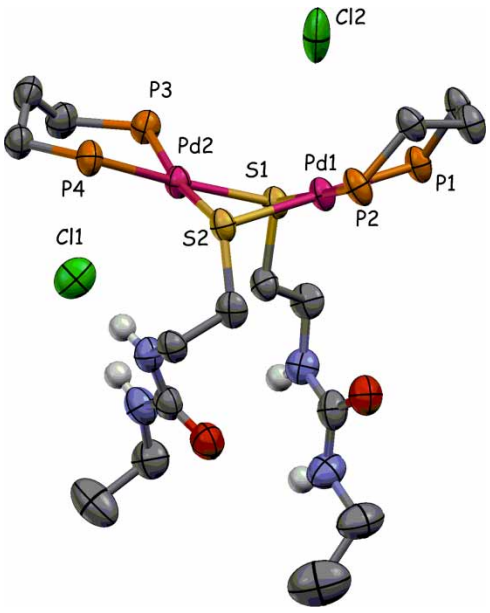


FIGURE 3 Ortep-Plot (thermal ellipsoids shown at 50% probability level) of **11**. Phenyl rings of the dppp ligands and the molecule's hydrogen atoms (except those of the urea groups) have been omitted for clarity.

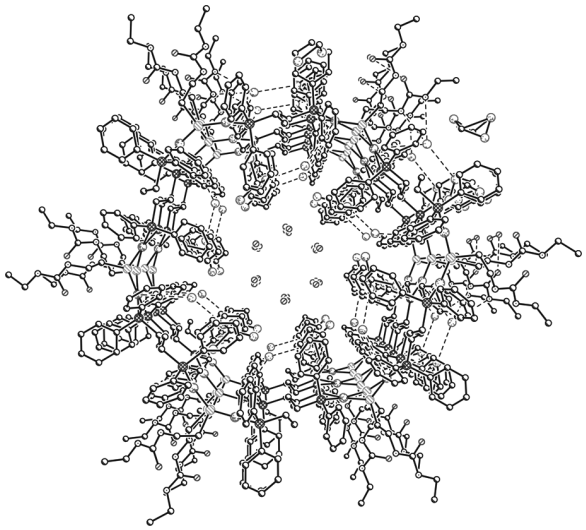


FIGURE 4 View along the c-axis of the helical arrangement observed in the crystal packing of **11**. The assembly gives rise to channels inside of which water molecules are found.

found in the crystal (see below). The chorine atoms are localised each at one side of the Pd_2S_2 ring. The closest distances to the metal centers are: Pd1···Cl2: 3.456 Å and Pd2···Cl1: 3.345 Å.

The crystals of **11** could be indexed in a hexagonal cell with the space $R\bar{3}$. In the crystal packing, neighboring molecules of the complex display supramolecular interactions yielding an interesting helical assembly with three molecules of **11** on each "level" of the helix (see Fig. 4). This helical arrangement leads to the formation of channels which contain partly disordered water molecules (the hydrogen atoms of which could not be localised).

Each helix connects with neighboring helices via hydrogen bonds between the urea groups of the thiolato ligands and a water molecule (see Fig. 5 and yellow background in Fig. 6). Additionally the helices are connected through weak interactions between the external phenyl rings of the phosphines and disordered dichloromethane molecules (green background in Fig. 6).

Solution Studies: Variable Temperature NMR and Anion Binding Studies

Once the structures of these di-palladium complexes were established, we turned our attention to their behaviour in solution. Since our aim is to use these as anion receptors, a detailed investigation of their conformation in solution was carried out. In particular, their ^1H and ^{31}P-{^1H} NMR spectra were analysed in more detail and computational studies were carried out to rationalise the observations.

The ^1H NMR spectra of these complexes demonstrated to be quite sensitive to the solvent employed in the measurement. For example, in d_6-DMSO or CH_3OD sharp and well-resolved spectra were

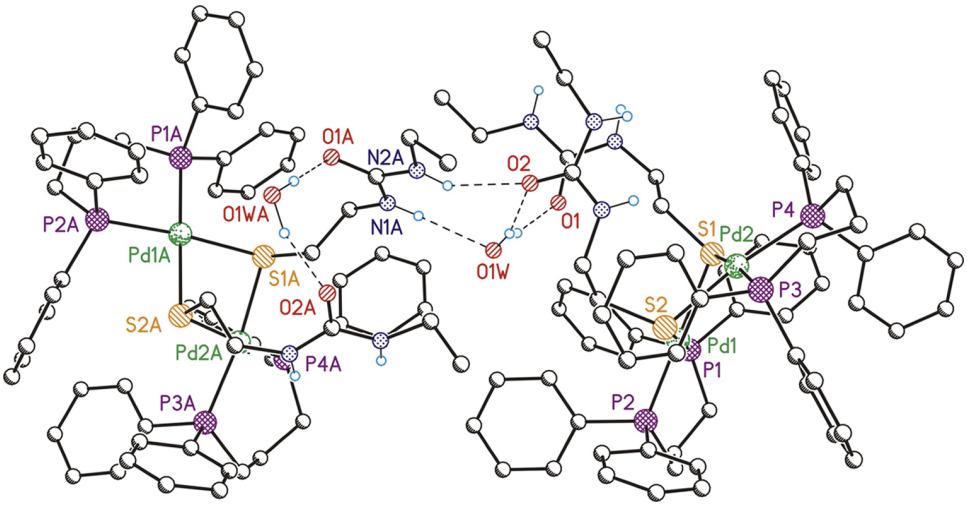


FIGURE 5 Molecular structure showing the hydrogen bonds between the urea groups and a water molecule. Distances: O1W···O1: 2.773(3) Å; O1W···O2: 2.781(3) Å; O1W···N1A: 3.038(4) Å; N2A···O2: 2.893(4) Å.

observed while broad and un-resolved spectra were obtained when non-protic solvents such as $CDCl_3$ were used. Also, we observed that addition of certain anions (see below) to solutions of the receptors sharpened and resolved the ^1H NMR signals.

These observations suggest that in solution the di-palladium complexes are in a conformational equilibrium which can be modified by the nature of the solvent or upon addition of anions (in particular those that are strongly bound by the receptors). A possible process consistent with these results would involve two conformations of the palladium dimers in which the thiolato-urea ligands are either both on the same side or one above and one below of the Pd_2S_2 plane of the complex (see Fig. 7).

To investigate this possibility, variable temperature $^{31}P\{^1H\}$ NMR spectra were recorded for **1**, **9** and **10** (see Fig. 8 for an example). The measurements were carried out in CD_3OD since this solvent provides a wide temperature range with melting point at $-97°C$ (176 K).

The singlet observed at room temperature splits into two as the temperature drops, suggesting that there is an equilibrium between two conformers with different phosphorous environments At low temperatures (<190 K) this equilibrium is slow enough to be detected by NMR spectroscopy. The spectrum measured at 290 K at the end of the experiment shows that the equilibrium is fully reversible.

Once the behaviour of the receptors in solution was established, their anion-binding properties were

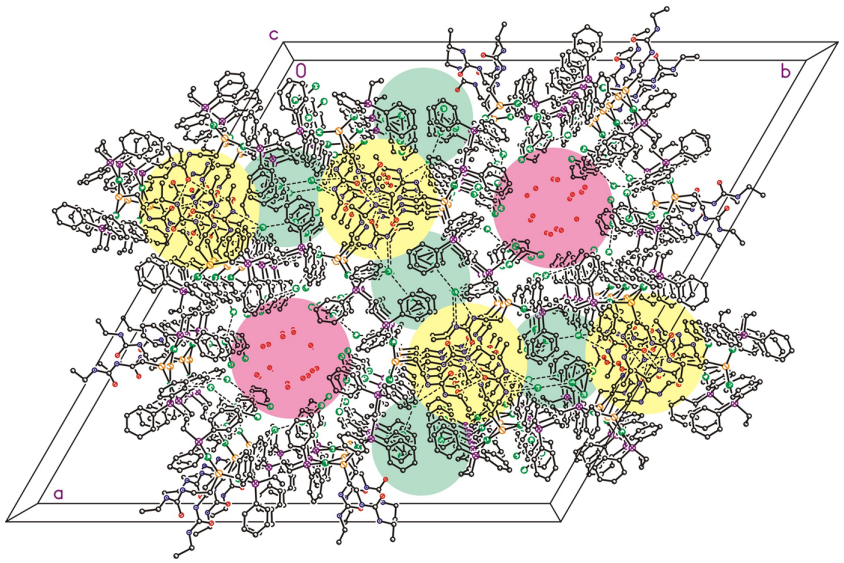


FIGURE 6 Crystal packing of **11** viewed along the c-axis. The areas where the water molecules are located inside the channels have been highlighted with a pink background. The regions of inter-helix contact (via hydrogen bonding between the thiolato ligands and water molecules) are highlighted with a yellow background. The areas where the dichloromethane molecules are located have been highlighted with a green background.

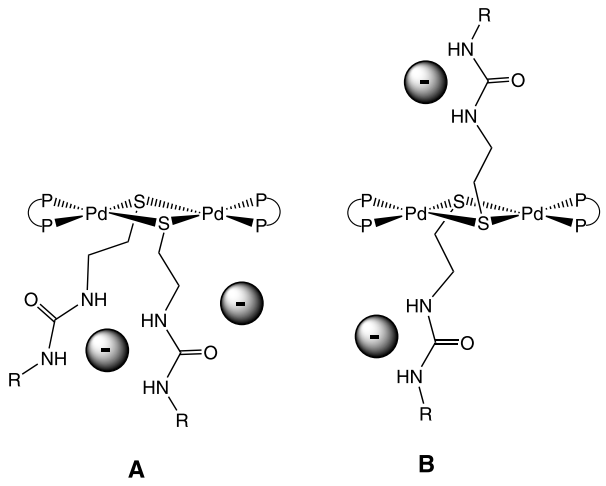


FIGURE 7 Two possible conformations of the thiolato-bridged complexes.

investigated by titrating the corresponding metallo-receptor (in DMSO) with different anions. The host–guest interactions were investigated by ^{1}H NMR spectroscopy recording the changes in chemical shift of the urea protons of the corresponding complex upon adding increasing amounts of the different anion. As reported in our preliminary communication, **1** demonstrated to be a good receptor for anionic species. The host–guest interactions were found to follow the trend: $[H_2PO_4]^- > [(PhO)PO_3H]^- > Br^- > Cl^- > [HSO_4]^- > > [PF_6]^-$ (with the largest association constant being $\log K_a = 3.5$ for $[H_2PO_4]^-$). It should be pointed out that the differences in K_a between **1** and the following anions: $[H_2PO_4]^-$, $[(PhO)PO_3H]^-$ and Br^- were very small. This indicates that, although **1** binds anions reasonably well in DMSO, its selectivity is limited. To investigate whether the new metallo-receptor **10** would show a higher degree of selectivity titration studies were carried out. Since receptor **1** showed to bind $[H_2PO_4]^-$, $[(PhO)PO_3H]^-$ and Br^- with relatively high binding constants but with little selectivity (see Table I), titrations of **10** were only carried out using these three anions. As can be seen in Table I, there is little discrimination between the three anions (as observed for **1**) and the binding constants are one order of magnitude smaller than with **1**. This is not surprising since ureas substituted with aromatic groups tend to bind anions more strongly than their aliphatic counterparts. Due to the lack of selectivity and smaller K_a values, no more anion binding studies were carried out using **10** as a receptor.

The binding constants between different anions and metallo-receptors **1** and **10** are larger than those reported in the literature for simple ureas (e.g., the association constant between the urea *Tol*-NHC(=O)NHBu and $[P(=O)(OH)(OPh)O]^-$ in DMSO has been reported [47] to be $27(\pm 4)\ M^{-1}$ in comparison to a value of $\sim 10^3\ M^{-1}$ for our metallo-receptors). This suggests that the palladium(II) centres in **1** and **10** play an important pre-organising role bringing the thiol-ureas in an optimal conformation for anion binding. In addition, there is also an electrostatic contribution due to the doubly charged nature of the metal centres.

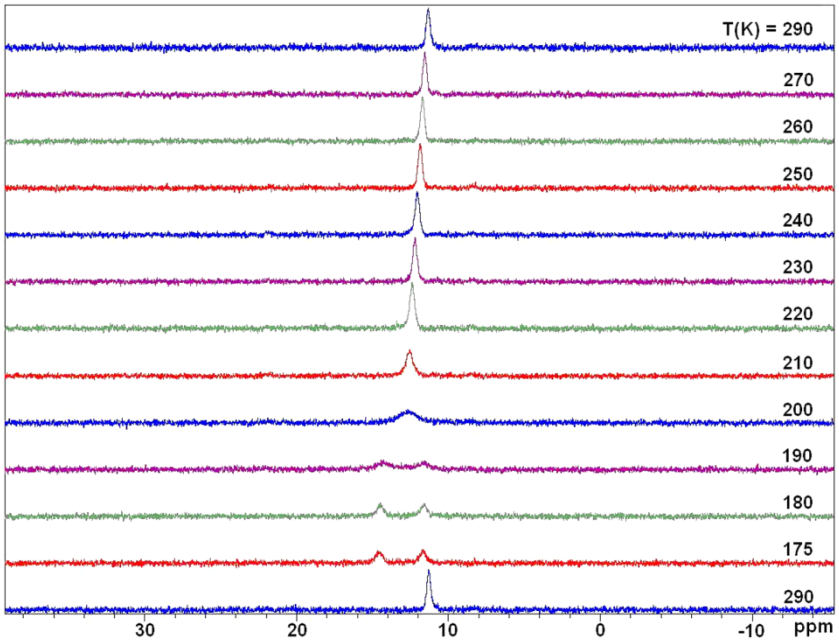


FIGURE 8 Section of the $^{31}P\{^1H\}$ NMR spectra of a solution of **10** in CD_3OD at different temperatures. The spectrum at the bottom corresponds to a measurement recorded at room temperature at the end of the experiment.

TABLE I Association constants (log K_a)† in DMSO solution

Anion	**1**‡ Log K_a (Std Dev¶)	**10** log K_a (Std Dev¶)
$[PF_6]^-$	~ 0	–
$[HSO_4]^-$	2.4 (± 0.05)	–
Cl^-	2.9 (± 0.05)	–
$[H_2PO_4]^-$	3.5 (± 0.08)	2.4 (± 0.21)
Br^-	3.3 (± 0.09)	2.8 (± 0.10)
$[P(=O)(OH)(OPh)O]^-$	3.4 (± 0.03)	2.6 (± 0.02)

† Determination of constants by ^1H NMR spectroscopy monitoring the changes in chemical shifts of the urea protons. ‡ The Ka values for metallo-receptor **1** were already reported in our preliminary communication [46]. ¶ Standard deviation corresponding to the fit of the experimental data to the calculated curve.

Computational Studies

In order to investigate in more detail the possible presence of the two different conformational isomers in solution (see Fig. 7 and discussion above), a computational study was carried out on one of the complexes (**1**, with R = Ph). Two isomers were computed; isomer A (Fig. 7) is the one observed in the solid state structures of **1** (and also in the structures of **9** and **11**). Geometrical parameters are quite similar to those of the X-ray structure, for instance, the four Pd-S distances are between 2.392 Å and 2.428 Å, and the triflate anions are in similar positions. In particular, this isomer has both of the thiolate ligands on the same side of the central Pd_2S_2 ring, as indicated by a C—S—S—C dihedral angle of 7.7°. An alternative conformation for the thiolato-bridged palladium dimers could be structure B (see Fig. 7) in which the two thiolato-urea substituents are pointing in opposite directions (one above and the other one below the Pd_2S_2 ring, with a C—S—S—C dihedral angle of 177.5°).

The relative energies of these two isomeric forms were analysed with different counteranions and in different environments. The results are reported in Table II. These results fit well with the experimental observation of two isomers (when $[CF_3SO_3]^-$ is the counteranion) found by NMR spectroscopy in solution. The two isomers have close energies both in THF (0.9 kcal/mol) and DMSO (1.2 kcal/mol). When the calculations are carried having Br^- or Cl^- as counterions, the energy difference between the two isomers is larger than 9 kcal/mol, which agrees with the experimentally observed sharpening of the peaks upon addition of anions.

TABLE II Relative energies (kcal/mol) of the isomeric forms A and B as a function of the counteranion and the solvent. Positive values indicate the A form to be more stable

	$[CF_3SO_3]^-$	None	Br^-	Cl^-
Vacuum	− 2.0	+ 8.8	+ 5.1	+ 5.5
THF	+ 0.9	− 3.3	+ 9.2	+ 9.1
DMSO	+ 1.2	− 6.4	+ 10.9	+ 10.5

Different trends can be observed in Table II that lead to a better understanding of these behaviours. The solvation effects seem to be related to polarity, with THF having always intermediate effects between those of vacuum and the more polar DMSO. In the absence of counterion, isomer A is more stable in vacuum than B (by 8.8 kcal/mol), but becomes less stable in solution (by − 3.3 kcal/mol in THF and − 6.4 kcal/mol in DMSO). The reason for this can be explained by the more open structure of B, allowing the urea groups to interact more easily with the solvent. The potential hydrogen bonds of the thiolato-urea ligands are more exposed in the B isomer, which is thus better stabilized by the solvent.

The effect of the solvent is the opposite when a counterion is present. In these cases, isomer A gains stability when adding the solvent effect. Again, a simple qualitative explanation can be found. In isomer A, one of the two anions is well surrounded by the hydrogen bonds from ligands, but the other is left practically unprotected, thus very sensitive to solvation. In isomer B, one anion is interacting with each "arm" of the complex, and the total solvation effect is smaller. The different behaviour of $[CF_3SO_3]^-$ and the halide ligands is finally not related to solvation, which has approximately the same effect for the three cases, but to intrinsic differences between the vacuum interactions with the host complex, which are more favourable for A in the case of triflate, probably because of the larger size of the anion. It seems thus clear that isomer B is the second species present in solution, and in equilibrium with the structure A, observed in the solid state.

Decomposition of the Complex

During the anion binding studies it was observed that if the metallo-receptors were left in solution for long periods of time, decomposition of the system took place. This was first suspected when a signal at 34 ppm was detected in the $^{31}P\{^1H\}$ NMR spectra of some samples throughout the titration experiments of **1** and **10**, in addition to the original singlet associated with the corresponding di-palladium compound (at ca. 11 ppm). Since the titrations were not carried out under strict anaerobic conditions, it would not be surprising that oxygen could eventually oxidise the dppp; the singlet at 34 ppm has in fact been assigned to this process since the value is comparable to that previously reported for he corresponding di-oxide of the phosphine ($O{=}PPh_2(CH_2)_3Ph_2P{=}O$, reported $^{31}P\{^1H\}$ NMR = 32.4 s).

The decomposition pathway described above was not the only one identified for the di-palladium complexes. Crystals grown from a solution of **9** in $CHCl_3$ revealed to be the unexpected product

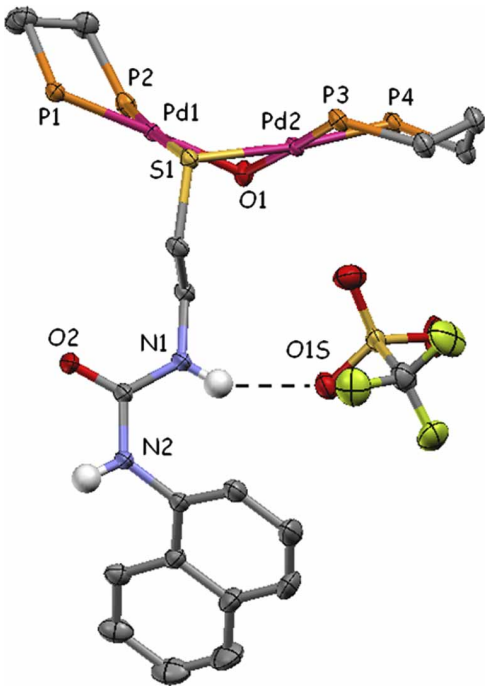


FIGURE 9 Ortep-plot (thermal ellipsoids shown at 50% probability level) of **12**. Phenyl rings of the dppp ligands and the molecule's hydrogen atoms (except those of the urea groups) have been omitted for clarity.

$[Pd_2(dppp)_2\{\mu\text{-}SCH_2CH_2NHC(=O)NH{-}Np\}(\mu\text{-}OH)][CF_3SO_3]_2$ (**12**) where a hydroxyl group has substituted one of the thiol-urea ligands originally present in **9**. The structure of this complex was unambiguously elucidated by single crystal X-ray structure analysis (see Fig. 9).

The metal atoms are bridged by one thiolate and one OH ligand (Pd···Pd: 3.1524(3) Å; Pd-S: 2.3794(5)/2.3667(4) Å; Pd-O: 2.0993(13)/ 2.0989(13) Å). The metal–metal separation is shorter than in the Pd_2S_2 complexes described above. In the unit cell compound **12** crystallises together with two triflate counterions, two molecules of tetrahydrofurane and a disordered water molecule with a half occupied position (hydrogen atoms could not be localised). In the crystal packing it can be observed that the complex is forming hydrogen bonded dimers connected via the urea groups (see Fig. 10). The triflate counter anions are positioned on opposite sides of the metal atoms, the shortest distances being: O1SA···Pd1: 3.90 Å and O2SB···Pd2: 3.04 Å.

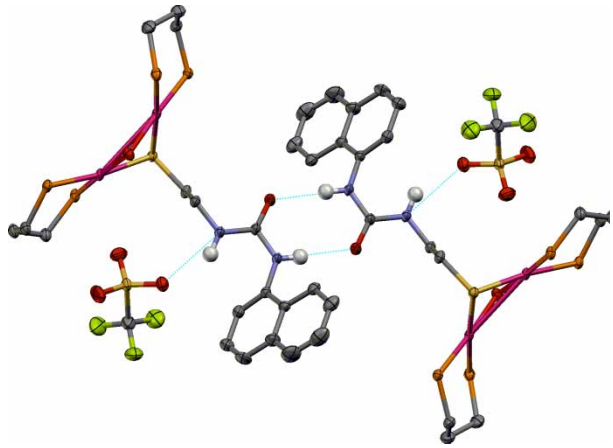


FIGURE 10 Molecular structure showing the dimer of **12** observed in the crystal packing. Distance of the symmetric hydrogen bonds: O2···N2A: 2.973(2) Å. Phenyl rings of the dppp ligands and the molecule's hydrogen atoms (except those of the urea groups) have been omitted for clarity.

CONCLUSIONS

A series of anion metallo-receptors based on di-palladium compounds bridged by thiolato-urea ligands have been prepared and fully characterised. Both solution and solid state studies have shown that these complexes do indeed bind anions even in competitive solvents such as DMSO. In spite of these encouraging results, the selectivity of the complexes for specific anions is not very good. This might be a consequence of the open and flexible structure of the metallo-receptors. The latter has been studied by NMR and computational methods showing that there are at least two possible conformations for these di-palladium complexes. Further studied will be required to investigate modifications to the thiolato ligands that could lead to more selective metallo-receptors. Changes in the length and flexibility of the spacer that links the sulfur atom and the urea groups are currently being investigated.

EXPERIMENTAL

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 by distillation from the appropriate drying agent, degassed and stored under nitrogen. Alternatively, solvents were dried using an "Innovative Technology" solvent purification system with alumina columns and, where appropriate, copper catalysts. All commercially available starting materials were not further purified unless otherwise stated. ^1H, ^{31}P, and ^{13}C NMR spectra were recorded on 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}. $Pd(dppp)Cl_2$ was synthesized by slight modifications of previously reported procedures. $Pd(dppp)(OTf)_2$ was prepared *in situ* by the reaction between $Pd(dppp)Cl_2$ and

$Ag(CF_3SO_3)$. Palladium complex **1** and thiol-urea ligand **2** were prepared as previously reported.

Synthesis of [Np-NHC(=O)NH(CH$_2$)$_2$S–]$_2$ (3)

$[-S(CH_2)_2NH_2]_2{\cdot}2HCl$ (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 (1-$C_{10}H_7$)NCO (3.2 ml, 22 mmol). The reaction mixture was stirred at 90°C overnight in the absence of light. After allowing the mixture to cool down to room temperature an off-white solid precipitated which was separated by filtration and washed with H_2O (2 × 50 ml) and Et_2O (2 × 50 ml) to afford the final product as a white powder. Yield: 3.55 g, 73%. IR (ν (KBr)): 3328, 3286 (N–H), 3052 (aromatic C–H), 2942 (aliphatic C–H), 1635, 1561 (C=O), 1501 (C=C). ^{1}H NMR (dmso-d_6) δ (in ppm) = 8.66 (s, 2H, NH), 7.4–8.1 (several signals, 14H, Ar-H), 6.87 (t, 2H, NH, $^3J_{NH-CH}$ = 5.5 Hz), 3.51 (dt, 4H, CH_2CH$_2$S, $^3J_{NH-CH}$ = 5.5 Hz, $^3J_{CH-CH}$ = 6.5 Hz), 2.93 (t, 4H, CH_2S, $^3J_{H-H}$ = 6.5 Hz). ^{13}C NMR (dmso-d_6) δ (in ppm) = 156.0 (C=O), 135.5 (1-Ar), 134.2 (5-Ar), 128.8 (6-Ar), 126.4 (7-Ar), 126.3 (3-Ar), 126.2 (8-Ar), 125.9 (10-Ar), 122.7 (9-Ar), 121.9 (4-Ar), 117.2 (2-Ar), 38.8 (C H$_2$CH$_2$S), 38.5 (CH_2S). FAB(+)-MS m/z (in a.m.u.): 491 (100%), $[M]^+$ (calcd 490.6); 245 (22%), $[C_{10}H_7NHCONH(CH_2)_2S]^+$ (calcd 245.3), 213 (7%), $[C_{10}H_7NHCONH(CH_2)_2]^+$ (calcd 213.3). UV (DMSO) λ_{max} = 309 nm ($\in$ = 1.853 × 10^4 cm^{-1} M^{-1}). Anal. Calcd. for $C_{26}H_{26}N_4O_2S_2$: C, 63.65; H, 5.34; N, 11.42. Found: C, 63.78; H, 5.51; N, 11.34.

Synthesis of [Et-NHC(=O)NH(CH$_2$)$_2$S–]$_2$ (4)

$[-S(CH_2)_2NH_2]_2{\cdot}2HCl$ (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 CH_3CH_2NCO (1.7 ml, 22 mmol). The reaction mixture was refluxed overnight, and then allowed to cool down to room temperature. A white solid precipitated which was separated by filtration and washed with H_2O (2 × 50 ml) and Et_2O (2 × 50 ml) to afford the final product as a white powder. Yield: 1.89 g, 64%. IR (ν (KBr)): 3341 (N–H), 2969, 2931 (C–H), 1626, 1584 (C=O). ^{1}H NMR (dmso-d_6) δ (in ppm) = 6.09 (t, 2H, NH, $^3J_{NH-CH}$ = 5.7 Hz), 6.01 (t, 2H, NH, $^3J_{NH-CH}$ = 5.7 Hz), 3.27 (dt, 4H, CH_2CH$_2$S, $^3J_{NH-CH}$ = 5.7 Hz, $^3J_{CH-CH}$ = 6.5 Hz), 3.00 (dq, 4H, CH_2CH$_3$, $^3J_{NH-CH}$ = 5.7 Hz, $^3J_{CH-CH}$ = 7.2 Hz), 2.73 (t, 4H, CH_2S, $^3J_{H-H}$ = 6.5 Hz), 0.98 (t, 6H, CH_3, $^3J_{CH-CH}$ = 7.2 Hz). ^{13}C NMR (dmso-d_6) δ (in ppm) = 163.3 (C=O), 44.0 (C H$_2$CH$_2$S), 43.9 (CH_2S), 39.5 (C H$_2$CH$_3$), 21.0 (CH_3). FAB(+)-MS m/z (in a.m.u.): 295 (100%), $[M]^+$ (calcd 294.5); 147 (35%), $[C_2H_5NHCONH(CH_2)_2S]^+$ (calcd 147.2); 115 (18%), $[C_2H_5NHCONH(CH_2)_2]^+$ (calcd 115.2). Anal. Calcd. for $C_{10}H_{22}N_4O_2S_2$: C, 40.73; H, 7.45; N, 18.74. Found: C, 40.79; H, 7.53; N, 19.03.

Synthesis of [Np-NHC(=O)NH(CH$_2$)$_2$S]$_2$Pb (5)

Compound **3** (2.533 g, 5.2 mmol), triphenylphosphine (2.708, 10.3 mmol) and $HCl_{(aq)}$ 37% (4 drops) were suspended in a degassed mixture of 1,4-dioxane (50 ml) and H_2O (8 ml) and stirred overnight at reflux under nitrogen, to reduce the disulfide bond to the corresponding thiol. After allowing the reaction mixture to cool down to ~40°C, $Pb(AcO)_2$ (2.154 g, 5.7 mmol) was added along with acetone (10 ml) to help it dissolve. A yellow precipitate formed within 20 min. The reaction mixture was stirred overnight at ~40°C after which time the yellow precipitate formed was isolated by filtration and washed with water (100 ml), acetone (2 × 50 ml) and diethyl ether (30 ml) to yield the final product. Yield: 3.30 g, 92%. IR (ν (KBr)): 3280 (N–H), 3047 (aromatic C–H), 2910 (aliphatic C–H), 1630, 1562 (C=O), 1502 (C=C). ^{1}H NMR (dmso-d_6) δ (in ppm) = 8.60 (s, 2H, NH), 7.4–8.3 (several signals, 14H, Ar-H), 6.76 (t, 2H, NH, $^3J_{NH-CH}$ = 5.5 Hz), 3.65 (t, 4H, CH_2S, $^3J_{H-H}$ = 6.3 Hz), 3.39 (dt, 4H, SCH_2CH_2, $^3J_{NH-CH}$ = 5.5 Hz, $^3J_{CH-CH}$ = 6.3 Hz). FAB(+)-MS m/z (in a.m.u.): 698 (<1%), $[M]^+$ (calcd 297.8). Anal. Calcd. for $C_{26}H_{26}N_4O_2PbS_2$: C, 44.75; H, 3.76; N, 8.03. Found: C, 44.64; H, 3.65; N, 7.93.

Synthesis of [Et-NHC(=O)NH(CH$_2$)$_2$S]$_2$Pb (6)

Compound **4** (0.588 g, 2.0 mmol), triphenylphosphine (1.049 g, 4.0 mmol) and $HCl_{(aq)}$ 37% (2 drops) were suspended in a degassed mixture of 1,4-dioxane (20 ml) and H_2O (4 ml) and stirred overnight at reflux under nitrogen, to reduce the disulfide bond to the corresponding thiol. After allowing the reaction mixture to cool down to ~40°C, $Pb(AcO)_2$ (0.759 g, 2.0 mmol) was added along with acetone (2 ml) to help it dissolve. A yellow precipitate formed within 10 min. The reaction mixture was stirred for one further hour after which time the yellow precipitate was separated by filtration and washed with water (20 ml), acetone (20 ml) and diethyl ether (2 × 20 ml) to yield the final product. Yield: 0.83 g, 83%. IR (ν (KBr)): 3323 (N–H), 2966, 2927 (C–H), 1620 (C=O). ^{1}H NMR (dmso-d_6) δ (in ppm) = 5.90 (m, 4H, NH), 3.61 (t, 4H, CH_2S, $^3J_{H-H}$ = 6.9 Hz), 3.15 (dt, 4H, CH_2CH$_2$S, $^3J_{NH-CH}$ = 5.9 Hz, $^3J_{CH-CH}$ = 6.9 Hz), 3.00 (dq, 4H, CH_2CH$_3$, $^3J_{NH-CH}$ = 5.9 Hz, $^3J_{CH-CH}$ = 7.2 Hz), 0.98 (t, 6H, CH_3, $^3J_{CH-CH}$ = 7.2 Hz). ^{13}C NMR (dmso-d_6) δ (in ppm) = 45.5 (C H$_2$CH$_2$S), 34.1 (C H$_2$CH$_3$), 27.7 (CH_2S), 15.7 (CH_3). FAB(+)-MS m/z (in a.m.u.): 502 (2%), $[M]^+$ (calcd 501.6); 355 (57%), $[C_2H_5NHCONH(CH_2)_2SPb]^+$ (calcd 354.4). Anal. Calcd.

for $C_{10}H_{22}N_4O_2S_2Pb{\cdot}2H_2O$: C, 22.34; H, 4.87; N, 10.42. Found: C, 22.03; H, 4.66; N, 10.53.

Synthesis of Np-NHC(=O)NH(CH$_2$)$_2$SH (7)

Pb{S(CH$_2$)$_2$NH(C=O)NH—Np}$_2$ (0.699 g, 1.0 mmol) was suspended in MeOH (30 ml) and 9 ml of a 0.24 M solution of HCl in MeOH (2.2 mmol) were added dropwise to the reaction to reach a pH around 1–2. The reaction mixture changed from light yellow to white within 10 min. After 2 hrs the suspended solid was filtered off and rinsed with $CHCl_3$ (3 × 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 × 20 ml) to eliminate excess of acid. Filtration and air drying produces final product as a white solid. Yield: 0.254 g, 51%. IR (ν (KBr)): 3313, 3278 (N—H), 3087, 3057 (aromatic C—H), 2939 (aliphatic C—H), 1633, 1566 (C=O), 1498 (C=C). ^{1}H NMR ($CDCl_3$) δ (in ppm) = 7.4–8.1 (several signals, 7H, Ar-H), 6.55 (broad, 2H, NH), 3.38 (t, 2H, CH_2CH$_2$S, $^3J_{CH-CH}$ = 6.4 Hz), 2.63 (dt, 4H, CH$_2$S, $^3J_{CH-CH}$ = 6.4 Hz, $^3J_{CH-SH}$ = 8.4 Hz), 1.21 (t, 1H, SH, $^3J_{CH-CH}$ = 8.4 Hz). ^{13}C NMR ($CDCl_3$) δ (in ppm) = 156.1 (C=O), 135.6 (1-Ar), 134.3 (5-Ar), 128.9 (6-Ar), 126.5 (3-Ar), 126.3 (7-Ar), 126.2 (10-Ar), 125.9 (8-Ar), 122.7 (9-Ar), 122.0 (4-Ar), 117.2 (2-Ar), 43.2 (*C*H$_2$CH$_2$S), 25.0 (CH$_2$S). FAB(+)-MS m/z (in a.m.u.): 246 (68%), $[M]^+$ (calcd 246.3); 213 (14%), $[C_{10}H_7NHCONH(CH_2)_2]^+$ (calcd 213.3). Anal. Calcd. for $C_{13}H_{14}N_2OS$: C, 63.39; H, 5.73; N, 11.37. Found: C, 63.56; H, 5.65; N, 11.07.

Synthesis of Et-NHC(=O)NH(CH$_2$)$_2$SH (8)

Pb{S(CH$_2$)$_2$NH(C=O)NH-Et}$_2$ (0.414 g, 0.8 mmol) was suspended in MeOH (30 ml) and 5 ml of a 0.33 M solution of HCl in MeOH (1.7 mmol) were added dropwise to the reaction. The reaction mixture changed from yellow–orange to white within 15 min. After 3.5 hrs the pH was adjusted at ca. 2, and then the suspended solid was filtered off and rinsed with $CHCl_3$ (2 × 15 ml). The filtrate was evaporated at reduced pressure to give a colourless oil. The $CHCl_3$ extracts were combined with the oily filtrate and washed with H_2O (3 × 15 ml) to eliminate excess of acid. The organic phase was dried over $MgSO_4$, filtered and the solvent evaporated to yield the final product as a white solid. Yield: 0.20 g, 83%. IR (ν (KBr)): 3327 (N—H), 2970, 2927 (C—H), 1624, 1589 (C=O). ^{1}H NMR ($CDCl_3$) δ (in ppm) = 4.78 (broad, 1H, NH), 4.32 (broad, 1H, NH), 3.37 (t, 2H, CH_2CH$_2$S, $^3J_{CH-CH}$ = 6.2 Hz), 3.20 (q, 2H, CH_2CH$_3$, $^3J_{CH-CH}$ = 7.2 Hz), 2.67 (dt, 2H, CH$_2$S, $^3J_{CH-CH}$ = 6.2 Hz, $^3J_{CH-SH}$ = 8.4 Hz), 1.34 (t, 1H, SH, $^3J_{CH-SH}$ = 8.4 Hz) 1.14 (t, 3H, CH$_3$, $^3J_{CH-CH}$ = 7.2 Hz). ^{13}C NMR ($CDCl_3$) δ (in ppm) = 157.8 (C=O), 43.3 (*C*H$_2$CH$_2$S), 35.2 (*C*H$_2$CH$_3$), 25.5 (CH$_2$SH), 15.4 (CH$_3$). FAB(+)-MS m/z (in a.m.u.): 149 (100%), $[M + H]^+$ (calcd 148.2). Anal. Calcd. for $C_5H_{12}N_2OS$: C, 40.51; H, 8.16; N, 18.90. Found: C, 40.40; H, 8.26; N, 18.70.

Synthesis of [(dppp)Pd-μ-(S(CH$_2$)$_2$NHC(=O)NH—Np)]$_2$[TfO]$_2$ (9)

Pd(dppp)Cl$_2$ (0.118 g, 0.2 mmol) and Ag(SO_3CF_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_3SO_3]$_2$ was added to a freshly prepared mixture of HS(CH$_2$)$_2$-NH(C=O)NH—Np (0.049 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 hrs changing colour from light yellow to orange. After this time it was filtered under dinitrogen to eliminate traces of palladium metal formed during the reaction. From this filtrate an aliquot (2 ml approx.) was spared for crystallisation. The rest of the filtrate was concentrated under reduced pressure down to a half its volume (*ca*. 10 ml). Hexane was added to the concentrated solution to precipitate the final product as a beige solid. This powder was separated by filtration, washed with hexane (10 ml), and dried under reduced pressure. Yield: 0.056 g, 61%. IR (ν (KBr)): 3406 (N—H), 3054 (aromatic C—H), 2925 (aliphatic C—H), 1618 (C=O). ^{1}H NMR (dmso-d$_6$) δ (in ppm) = 6.93–8.09 (several signals, 54H, ArH), 6.36 (m, 2H, S(CH$_2$)$_2$N*H*), 2.90 (m, 4H, SCH$_2$C*H*$_2$), 2.53 (m, 4H, SCH$_2$). ^{31}P NMR ($CDCl_3$) δ (in ppm) = 11.4 (s). FAB(+)-MS m/z (in a.m.u.): 1826 (2%) $[M]^+$ (calcd 1826.5); 1677 (98%), $[M-(CF_3SO_3)]^+$ (calcd 1677.4); 1528 (32%), $[M-(CF_3SO_3)_2]^+$ (calcd 1528.4). UV (CH$_2$-Cl$_2$) λ_{max} = 230 nm ($\in_{230} = 1.90 \times 10^4\,cm^{-1}M^{-1}$), λ_{max} = 300 nm ($\in_{300} = 1.03 \times 10^4\,cm^{-1}\,M^{-1}$), λ_{max} = 345 nm ($\in_{345} = 4.7 \times 10^3\,cm^{-1}M^{-1}$). Anal. Calcd. for $C_{82}H_{78}F_6N_4O_8P_4Pd_2S_4$ ·THF: C, 54.40; H, 4.57; N, 2.95. Found: C, 54.25; H, 4.25; N, 3.28. Single crystals suitable for X-ray crystallographic studies were obtained by slow diffusion of hexane into the reaction mixture containing the crude product.

Synthesis of Na{[(dppp)Pd-μ-(S(CH$_2$)$_2$NHC(=O)NHC$_2$H$_5$)]$_2$[TfO]$_3$} ([10][NaOTf])

Pd(dppp)Cl$_2$ (0.118 g, 0.2 mmol) and Ag(SO_3CF_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_3SO_3]$_2$ was added to a freshly prepared mixture of HS(CH$_2$)$_2$-NH(C=O)NHC$_2$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 2 hours changing colour 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). Hexane was added to the concentrated solution and the product precipitated out of solution. The resulting yellow solid was separated by filtration, washed with hexane (10 ml), and dried under reduced pressure. Yield: 0.071 g, 39%. IR (ν (KBr)): 3395 (N-H), 3057 (aromatic C-H), 2932 (aliphatic C-H), 1653 (C═O). ^{1}H NMR (dmso-d_6) δ (in ppm) = 7.46 (t, 8H, p-ArH, $^3J_{p-m} = 7.4$ Hz), 7.39 (broad, 16H, *o*-ArH), 7.32 (t, 16H, *m*-ArH, $^3J_{p-m} = 7.4$ Hz), 5.68 (t, 2H, NH, $^3J_{NH-CH} = 5.6$ Hz), 5.23 (t, 2H, NH, $^3J_{NH-CH} = 6.2$ Hz), 2.90 (m, 12H, CH_2CH_2S and CH_2CH_3), 1.88 (m, 4H, SCH_2), 1.74 (m, 8H, PCH_2), 1.65 (broad, 4H, PCH_2CH_2), 0.90 (t, 6H, CH_3, $^3J_{CH-CH} = 7.2$ Hz). ^{13}C NMR (dmso-d_6) δ (in ppm) = 157.2 (C═O), 133.2 (*o*-Ar), 131.6 (*i*-Ar), 128.9 (*m*,*p*-Ar), 46.3 (CH_2CH_2S), 34.0 (CH_2CH_3), 22.6 (CH_2S), 21.4 ($PCH_2CH_2CH_2P$), 15.6 (CH_3). ^{31}P NMR ($CDCl_3$) δ (in ppm) = 11.1 (s). FAB(+)-MS m/z (in a.m.u.): 1481 (2%), [**10**—(CF_3SO_3)]$^+$ (calcd 1481.2); 665 (12%), [**10**—$(CF_3SO_3)_2$]$^{2+}$ (calcd 666.1). Anal. Calcd. for $C_{67}H_{74}F_9N_4NaO_{11}P_4Pd_2S_5$: C, 44.65; H, 4.14; N, 3.11. Found: C, 44.11; H, 4.14; N, 3.20.

Synthesis of [(dppp)Pd-μ-(S(CH$_2$)$_2$NHC(═O)NH-Et)]$_2$[Cl]$_2$ (11)

$Pd(dppp)Cl_2$ (0.059 g, 0.1 mmol) and $Pb(S(CH_2)_2NH(C{=}O)NH\text{-}Et)_2$ (0.050 g, 0.1 mmol) were suspended in dry CH_2Cl_2 (10 ml) under a dinitrogen atmosphere. The reaction mixture was stirred at 50°C for 24 hrs and the solid $PbCl_2$ formed was filtered off. A small aliquot (2 ml) of the resulting filtrate was spared for crystallisation. Hexane (20 ml) was added to the rest of the filtrate and the product precipitated out of solution. The resulting yellow solid was separated by filtration, washed with hexane (2 × 10 ml), and dried under reduced pressure. Yield: 0.039 g, 78%. IR (ν (KBr)): 3442 (N—H), 3051 (aromatic C—H), 2965, 2927 (aliphatic C—H), 1647 (C═O), 1435 (dppp), 1261 (dppp). ^{1}H NMR ($CDCl_3$) δ (in ppm) = 7.66 (broad, 16H, ArH), 7.37 (broad, 24H, ArH), 6.00 (broad, 2H, NH), 5.75 (broad, 2H, NH), 3.37 (broad, 4H, SCH_2CH_2), 3.13 (m, 4H, CH_2CH_3), 2.11 (broad, 4H, SCH_2), 1.92 (br, 8H, PCH_2), 1.27 (m, 4H, PCH_2CH_2), 1.13 (t, 6H, CH_3, $^3J_{CH-CH}$ = 7.2 Hz). ^{31}P NMR ($CDCl_3$) δ (in ppm) = 11.3 (s). ES(+)-MS m/z (in a.m.u.): 1445 (2%), [M + K]$^+$ (calcd 1442.2); 666 (100%), [(Pd(dppp)-μ-SR)$_2$]$^{2+}$ (calcd 666.1). Anal. Calcd. for $C_{64}H_{74}Cl_2N_4O_2P_4Pd_2S_2$?H_2O $(CH_2Cl_2)_2$: C, 49.83; H, 5.07; N, 3.52. Found: C, 49.02; H, 5.42; N, 3.87. Single crystals suitable for X-ray crystallographic studies were obtained by slow diffusion of hexane into the reaction filtrate aliquot containing final crude product.

Synthesis of [(dppp)$_2$Pd$_2$-μ-(S(CH$_2$)$_2$NHC(═O)NH—Np)-μ-(OH)][TfO]$_2$ (12)

Crystallisation of complex **9** by slow diffusion of hexane to a solution of the compound in THF yielded single crystals. An X-ray crystallographic analysis of one of these crystals revealed it to be a compound of **12**. IR (ν (KBr)): 3388 (broad N—H, and O—H), 3056 (aromatic C—H), 2926 (aliphatic C—H), 1686 (C═O). ^{1}H NMR ($CDCl_3$) δ (in ppm) = 7.36–8.21 (several signals, 47H, ArH), 6.55 (br, 1H, $S(CH_2)_2NH$). ^{31}P NMR ($CDCl_3$) δ (in ppm) = 19.5 (d, $^3J_{P-P}$ = 26 Hz), 8.4 (d, $^3J_{P-P}$ = 26 Hz). ESI(+)-MS m/z (in a.m.u.): 722 (5%), [(dppp)$_2$Pd$_2$(**15**)(OH)(CF_3SO_3)]$^{2+}$ (calcd 724.5).

Computational Details

Calculations in vacuum were carried out with the two-layer ONIOM(B3LYP:UFF) method [48,49] as implemented in the Gaussian03 program [50]. The MM description, with the UFF force field [51], was used for the phenyl rings, with all other atoms in the QM region, described at the Becke3LYP method [52,53]. For the geometry optimization, the LANL2DZ description was used for palladium, supplemented with an f shell (exponent of 1.472) and the 6–31G(d) basis set for all other atoms. Relative energies in vacuum were refined through single-point calculations with a larger 6–31G + (d) basis set for atoms different from palladium. The solvation effects were introduced through single point Becke3LYP calculations with the LACVP* basis set on the QM region of the optimized ONIOM structures using the Poison-Boltzmann method [54] as implemented in the Jaguar 5.5 program [55].

X-ray Crystallography

See Table III for details. The measured crystals were prepared under inert conditions immersed in perfluoropolyether as protecting oil for manipulation. *Data Collection*. Measurements were made on a Bruker-Nonius diffractometer equipped with a APPEX 2 4K CCD area detector, a FR591 rotating anode with $Mo_{K\alpha}$ radiation, Montel mirrors as monochromator and a Kryoflex low temperature device ($T = -173$°C). Full-sphere data collection was used with ω and ϕ scans. *Programs used*: Data collection Apex2 V. 1.0-22 (Bruker-Nonius 2004), data reduction Saint + Version 6.22 (Bruker-Nonius 2001) and absorption correction SADABS V. 2.10 (2003). *Structure Solution and Refinement*. SHELXTL Version 6.10 was used [56]. CCDC 632838 - 632840 contains the supplementary crystallographic data for

TABLE III Crystal data for compounds **9**, **11** and **12**

Compound	**9**	**11**	**12**
Formula	$C_{82}H_{78}F_6N_4O_8P_4Pd_2S_4$	$C_{64}H_{74}Cl_2N_4O_2P_4Pd_2S_4$	$C_{69}H_{66}F_6N_2O_8P_4Pd_2S_3$
Solvent detected	2/3 H_2O and 2 THF	2 H_2O and 2 $C_2H_2Cl_2$	$\frac{1}{2}$ H_2O and 2 THF
Formula weight	1981.29	1608.86	1750.31
Crystal size (mm^3)	0.4 × 0.4 × 0.2	0.40 × 0.05 × 0.02	0.2 × 0.2 × 0.1
Crystal color	Colorless	Colorless	Colorless
Temp (K)	100	100	100
Crystal system	Monoclinic	Hexagonal	Triclinic
Space group	*Pc*	$R\bar{3}$	$P\bar{1}$
A (Å)	25.393(3)	51.441(7)	12.5517(13)
B (Å)	14.1986(16)	51.441(7)	17.0631(18)
C (Å)	25.617(3)	14.922(4)	17.9116(18)
α (deg)	90	90	90.410(3)
β (deg)	92.184(2)	90	91.624(3)
γ (deg)	90	120	90.750(3)
V ($Å^3$)	9229.2(18)	34196(11)	3834.2(7)
Z	4	18	2
ρ (g/cm^3)	1.426	1.406	1.516
μ (mm^{-1})	0.620	0.869	0.708
θ_{max} (°)	27.20	25.38	39.64
Reflec. measured	133332	94367	76471
Unique reflections	63706 [$R_{int} = 0.0458$]	14458 [$R_{int} = 0.$ 0.1522]	42614 [$R_{int} = 0.0269$]
Obs. Reflec. Fo > 4σ(Fo)	49532	9427	32786
Absorption correction	SADABS (Bruker)	SADABS (Bruker)	SADABS (Bruker)
Trans. min/max	0.65315/1.00000	0.66139/1.00000	0.67689/1.00000
Parameters	2183	870	946
R1/wR2 [I > 2σ(I)]	0.0563/ 0.0778	0.0902/ 0.1380	0.0476/ 0.0648
R1/wR2 [all data]	0.1469/ 0.1622	0.2188/ 0.2490	0.1311/ 0.1415
Goodness-of-fit (F^2)	1.019	1.087	1.046
Peak/hole ($e/Å^3$)	2.049/ −1.393	1.612/−1.216	2.377/− 3.185

this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB21EZ, UK; (fax: (+44) 1223-336-033; or . E-mail: deposit@ccdc.cam.ac.uk).

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