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Anion templated synthesis of Ni/Pd containing metalla-macrocycles

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The anion templated synthesis of the nickel/palladium-based metalla-macrocycles $[Pd_2Ni_2(atu)_4(PPh_3)_4X]^{3+}$ (X = Cl, **1**; Br, **2**; I, **5**; atu = deprotonated amidinothiourea) is reported. In the presence of other anions such as $CF_3SO_3^-$ or NO_3^- the formation of the simple complex $Pd(Hatu)X_2$ (X = $CF_3SO_3^-$ or NO_3^-) is observed. Structural characterisation of two of the mixed-metal compounds (**1** and **2**, where X = Cl and Br respectively) confirmed square arrangements for the metalla-macrocycles and revealed some interesting features in the molecular structure of the species. The encapsulated anions inside the metalla-macrocycles have been demonstrated to be mobile in solution and halide exchange reactions have been carried out.

The planned and controlled synthesis of metalla-supramolecular arrays is an area that has attracted great interest over the past few years. The superstructures formed promise to have applications in a wide variety of areas such as catalysis,[1] new materials,[2] molecular transport[3] and molecular recognition.[4] One of the most successful approaches to the synthesis of metalla-supramolecular systems has been by templated self-assembly processes. Templating agents usually make use of non-covalent interactions such as electrostatic forces, H-bonding, π–π interactions and hydrophobic effects to pre-arrange the building blocks in a suitable geometry for the superstructures to be formed.[5] Most of the templating agents used by synthetic chemists are either cationic[6] or neutral species.[7] Anions, on the other hand, have only fairly recently been successfully utilised as templates.[8] This limited application has been attributed to the more diffuse nature (small charge to radius ratio), pH sensitivity and the relatively high solvation free energy of the anions employed.[9]

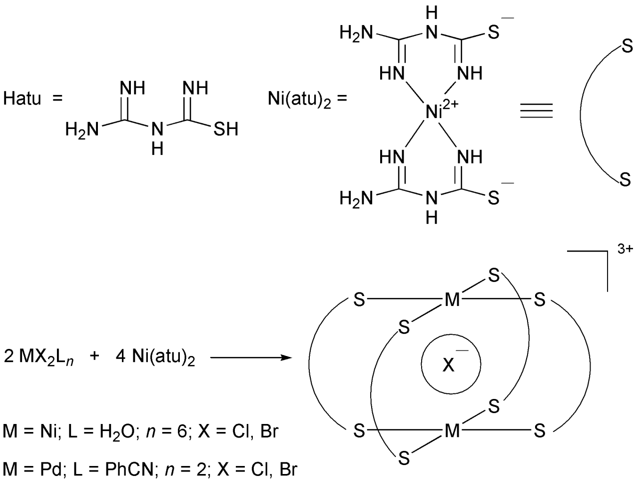
To date few examples of anion directed assemblies have been reported. Among the first metal-containing supramolecular assemblies synthesised by an anionic directed process were Hawthorne's mercuracarborands in which Lewis acid–base interactions between halides and mercury were responsible for the templating effect.[10] Around the same time Müller *et al.* postulated the templating role of various anions in the synthesis of a series of polyoxometallate clusters.[11] One of the most striking examples of anionic templated self-assembly are the metal–polypyridine double helicates of Lehn and co-workers.[12] Fujita and co-workers have reported the anionic directed synthesis of palladium cage-like structures and of coordination nanotubes.[13] Other recent examples of anion directed assemblies include a tetranickel box-type structure reported by Dunbar and co-workers,[14] the self-assembled circular structures reported by Ward and co-workers,[15] and the hexanuclear-silver cage by Mingos and James.[16]

Recently we reported a unique example of anionic directed self-assembly in which chloride and bromide selectively template the formation of a series of metallo-cages.[17] Based on these results, we embarked on a systematic study of the templating role of anions in the syntheses of a wide range of related metalla-cages and macrocycles. Here we report the anion-templated synthesis of a series of palladium and nickel containing metalla-macrocycles.

Results and discussion

Anion-directed synthesis of $[Pd_2Ni_2(atu)_4(PPh_3)_4X]^{3+}$ (X = Cl, 1; Br, 2)

In two previous communications[17,18] we have reported the use of $Ni(atu)_2$ (Hatu = amidinothiourea; atu = deprotonated form of Hatu), as a building block for the synthesis of a series of metallo-cages (see Scheme 1). This moiety proved to be a particularly good building block because of its combination of sulfur donor atoms and the presence of several NH groups for either additional metal coordination or for H-bonding.



Scheme 1

However, one of the problems we have encountered when studying the metallo-cages shown in Scheme 1 is that they have low solubility and are thus difficult to characterise spectroscopically. Moreover, once the molecular cages have been formed, the templating anions remain tightly encapsulated inside the superstructures preventing them from being removed or exchanged for other species. As a consequence, these cages have limited applications as molecular hosts (with potential applications in molecular recognition and sensing). In an attempt to resolve these three problems (*i.e.* solubility, characterisation and easy accessibility to the anion) the metalla-macrocycles shown in Scheme 2 have been investigated.

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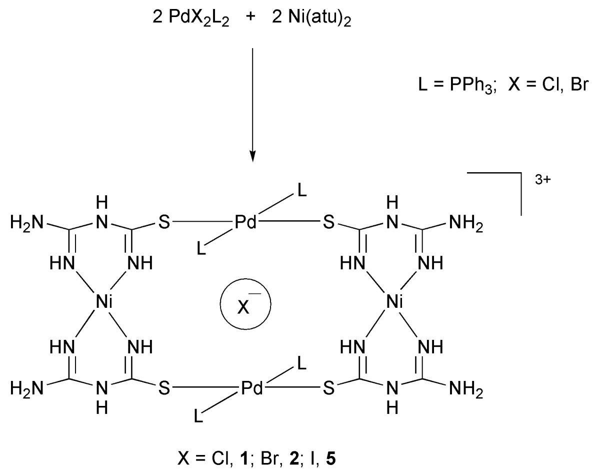


Scheme 2

When one equivalent of *trans*-Pd$(PPh_3)_2Cl_2$ was mixed with one equivalent of Ni$(atu)_2$ [prepared *in situ* from Ni$(ClO_4)_2$ and two equivalents of Hatu] a clear orange solution was obtained. The $^{31}P\{^1H\}$ NMR spectrum of the reaction mixture showed a singlet at δ 22.0 (which is at a slightly higher field than the chemical shift of the starting material). After two hours (during which time no further changes in the $^{31}P\{^1H\}$ NMR spectrum were observed) an orange solid was isolated by addition of diethyl ether to the reaction mixture. On the basis of IR, $^{31}P\{^1H\}$ NMR spectroscopy and elemental analyses this solid was formulated as $[Pd_2Ni_2(atu)_4(PPh_3)_4Cl][ClO_4]_2Cl$ **1**. This formulation was confirmed by an X-ray diffraction study of single crystals of **1** obtained by layering an ethanolic solution of **1** with hexane. The replacement of two of the Ni$(atu)_2$ units by four PPh_3 groups results in a solid state structure (Fig. 1) very similar to that adopted by $[Pd_2Ni_4(atu)_8Cl]Cl_3$ **3**.[18]

The molecule retains a cage-like structure possessing crystallographic C_2 symmetry with the chloride ion encapsulated at its centre. Although this structure does not have the rigid constraints of **3**, the role of the two "missing" Ni$(atu)_2$ units is, to some extent, mimicked by the inwardly directed phenyl rings of the PPh_3 ligands. The chloride ion is bound primarily by the four N–H $\cdots$ Cl hydrogen bonds from the inwardly directed atu N–H groups (H $\cdots$ Cl distances of 2.46 and 2.54 Å with associated N–H $\cdots$ Cl angles of 175 and 162°) and, to a much lesser extent, by six near-linearly directed C–H $\cdots$ Cl interactions from *ortho* hydrogen atoms of the PPh_3 phenyl rings (the H $\cdots$ Cl distances range between 2.85 and 3.08 Å with C–H $\cdots$ Cl angles of between 162 and 168°). The PdP_2S_2 coordination geometry is distinctly distorted square planar, with the palladium atom being displaced by 0.43 Å out of the "basal" plane in the direction of the encapsulated chloride ion (compared to 0.31 Å in **3**). This distortion reflects the interaction between the guest anion and the metal axial d_{z^2} orbital; the Pd $\cdots$ Cl distance, 3.267(1) Å, is however *ca.* 0.1 Å *longer* than in **3**. A possible reason for these seemingly contradictory differences is that the bulk of the triphenylphosphine ligands limits the degree to which the Ni$(atu)_2$ units can cant relative to the Pd $\cdots$ Pd axis of the molecule. This results in the Pd $\cdots$ Pd separation being greater, and hence in order to maintain the Pd $\cdots$ Cl interaction, the palladium atom has to be displaced more out of the plane of its four substituents. Evidence to support this argument is found in the degree of rotation of the upper and lower PdP_2S_2 units with respect to each other which here is 44° (*i.e.* almost perfectly staggered, Fig. 2) whereas in **3** the twist is 73°.

The Ni$(atu)_2$ units adopt a folded conformation similar to that of the parent Ni$(atu)_2$ complex.[18] The Pd–S and Ni–N coordination distances do not differ significantly from those in **3**, and the Pd–P distances are unexceptional (Table 1). In addition to the N–H $\cdots$ Cl and C–H $\cdots$ Cl interactions described above, the complex is further stabilised by a pair of symmetry related stacking interactions between one of the phenyl rings and its proximal atu ligand [that containing N(7)]; the shortest associated atom $\cdots$ atom contact is 3.40 Å. There is also an edge-to-face aromatic $\cdots$ aromatic interaction between a pair of P(1) and P(2) phenyl rings (uppermost in Figure 1), the centroid $\cdots$ centroid separation being 5.03 Å with the rings being inclined by 81°. The outwardly directed atu N–H groups lie within hydrogen bonding distance of oxygen atoms of the (disordered) perchlorate anions. There are no complex $\cdots$ complex interactions of note.

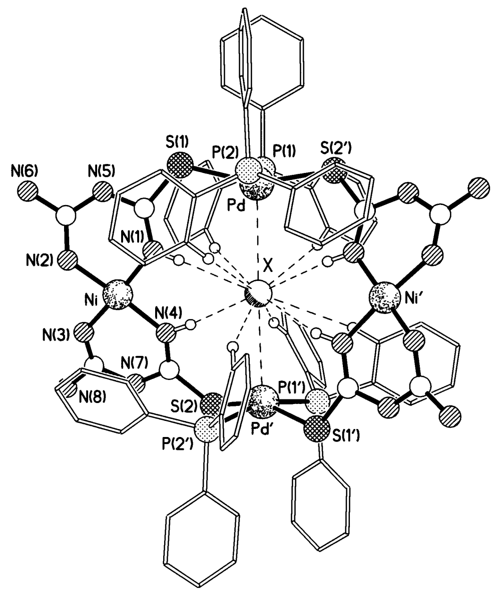


Fig. 1 The molecular structure of **1** (X = Cl). N–H $\cdots$ X hydrogen bonding geometries [N $\cdots$ X, H $\cdots$ X distances (Å) and N–H $\cdots$ X angle (°)]. For **1** (X = Cl); 3.41, 2.54, 162; 3.36, 2.46, 175. For **2** (X = Br): 3.51, 2.64, 163; 3.48, 2.59, 171; 3.47, 2.58, 172; 3.48, 2.61, 165.

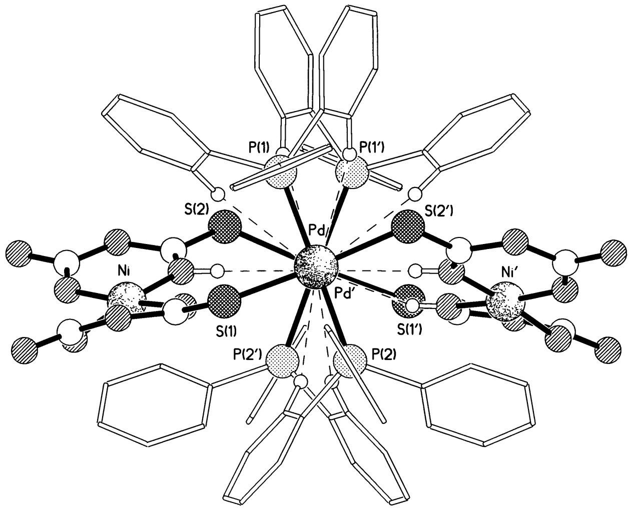


Fig. 2 View down the Pd $\cdots$ Cl $\cdots$ Pd axis in **1** showing the staggering of the upper and lower PdP_2S_2 units and the folding of the Ni$(atu)_2$ moieties.

A similar synthetic procedure to the one used to synthesise **1**, was followed to prepare the bromide analogue **2**. A mixture of *trans*-Pd$(PPh_3)_2Br_2$ and Ni$(atu)_2$ was reacted for two hours and, upon addition of diethyl ether, a bright orange compound was precipitated. On the basis of IR, $^{31}P\{^1H\}$ NMR spectroscopy and elemental analyses this solid was characterised as $[Pd_2Ni_2(atu)_4(PPh_3)_4Br][ClO_4]_2Br$ **2**.

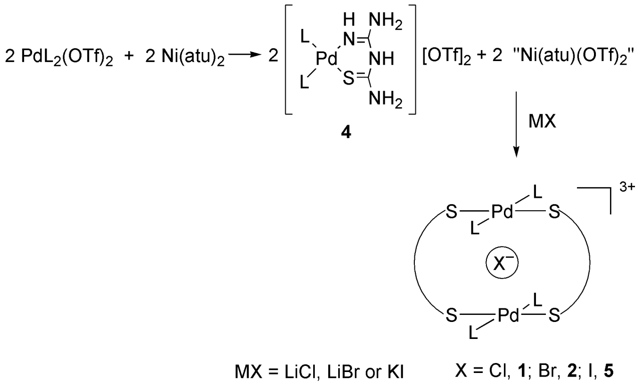
The fact that the chloride is tightly bound *via* H-bonds and Lewis acid–base interactions to the metalla-macrocycle **1** suggests that it is acting as a templating agent for its synthesis (and similarly the bromide for the synthesis of **2**). However,

Table 1 Selected bond lengths (Å) and angles (°) for **1** (X = Cl) and **2** (X = Br)

	1 (X = Cl)	**2** (X = Br)		**1** (X = Cl)	**2** (X = Br)
Pd–S	2.320(2) 2.332(3)	2.336(2) 2.338(3) 2.340(3) 2.345(3)	Pd–P	2.341(2) 2.351(2)	2.335(3) 2.342(3) 2.347(3) 2.358(3)
Ni–N(inside)	1.867(9) 1.885(8)	1.865(8) 1.868(8) 1.879(8) 1.884(8)	Ni–N(outside)	1.846(13) 1.851(10)	1.832(9) 1.847(9) 1.855(9) 1.870(8)
S–Pd–P	86.15(8) 86.22(9) 88.02(9)	83.42(9) 85.18(10) 85.32(10)	S–Pd–S	157.14(10)	149.93(9) 150.91(10)
	91.97(9)	86.55(10) 88.82(11) 90.92(9) 90.74(10) 90.94(10)	P–Pd–P	160.48(9)	161.54(9) 162.86(10)

further evidence was deemed necessary to unambiguously demonstrate the templating role of both these anions. Thus, the reaction between $Pd(PPh_3)_2(CF_3SO_3)_2$ and $Ni(atu)_2$ was studied. The internal dimensions of macrocycle **1** (revealed by the X-ray structure) are clearly not sufficiently large to accommodate anions such as triflate. As a consequence, if the synthesis of the metalla-macrocycles is really directed by small and spherical anions such as chloride and bromide, the reaction in the presence of triflate should not lead to the formation of the macrocycle.

One equivalent of $Pd(PPh_3)_2(CF_3SO_3)_2$ in tetrahydrofuran was mixed with one equivalent of $Ni(atu)_2$ in methanol [prepared *in situ* from $Ni(ClO_4)_2$ and Hatu] and the reaction mixture was monitored by $^{31}P\{^1H\}$ NMR spectroscopy. A few minutes after the reagents were mixed, the original singlet at δ 36.1 due to $Pd(PPh_3)_2(CF_3SO_3)_2$, disappeared and the formation of a new pair of doublets at δ 32.4 and 30.5 was observed. The reaction was left stirring for one more hour during which time no further changes were observed leaving the pair of doublets as the only phosphorus-containing product. This clearly indicated that a macrocycle analogous to **1** and **2** had not been formed since in these products all the phosphine ligands should be equivalent (and hence a singlet in the $^{31}P\{^1H\}$ NMR should be observed). In order to establish the nature of the new product, diethyl ether was added to the reaction mixture to separate a yellow precipitate. The $^{31}P\{^1H\}$ NMR spectrum of this species showed the pair of doublets previously seen in the reaction mixture (an AB pattern). On the basis of $^{31}P\{^1H\}$ NMR, IR and FAB-mass spectrometry, this product was formulated as $[Pd(PPh_3)_2(Hatu)](OTf)_2$ **4** (see Scheme 3).



Scheme 3

This product was also obtained by reacting one equivalent of $Pd(PPh_3)_2(CF_3SO_3)_2$ with one equivalent of amidinothiourea. Since atu is an asymmetric ligand, the two phosphine ligands become inequivalent, coupling to each other and giving rise to the observed AB pattern.

These results strongly suggest that the presence of chloride or bromide is essential for the formation of the corresponding metalla-macrocycles. In order to confirm this observation, a new experiment was carried out. After $Pd(PPh_3)_2(CF_3SO_3)_2$ and $Ni(atu)_2$ had been reacting for two hours (and the $^{31}P\{^1H\}$ NMR spectrum of the reaction mixture showed only the AB pattern corresponding to **4**), stoichiometric amounts of chloride were added. Minutes after the addition, the $^{31}P\{^1H\}$ NMR spectrum of the mixture showed the appearance of a singlet at δ 22.0 which indicated that the metalla-macrocycle **1** was being formed. After two hours the $^{31}P\{^1H\}$ NMR spectrum showed that most of **4** had been converted to **1**. A similar experiment was carried out by adding bromide to a mixture of $Pd(PPh_3)_2(CF_3SO_3)_2$ and $Ni(atu)_2$. In this case $^{31}P\{^1H\}$ NMR spectroscopy showed that **4** had converted to **2**. In order to confirm that the shifts in the NMR spectrum were indeed due to the metalla-macrocycles **1** and **2**, diethyl ether was added to the corresponding reaction mixtures and the orange solids obtained were fully characterised (as the metalla-macrocycles) by $^{31}P\{^1H\}$ NMR, IR spectroscopy and elemental analyses. Further confirmation that the metalla-macrocycles were formed by this procedure was obtained by a structural characterisation of **2**.

Crystals suitable for an X-ray crystallographic analysis were obtained by layering an ethanolic solution of **2** with hexane. The structure of the bromide-containing metalla-macrocycle **2** is little different from that of its chloride analogue **1** (Fig. 1), though here the molecule has only approximate molecular C_2 symmetry. The bromide anion is positioned virtually at the centre of the metalla-macrocycle, with Pd···Br distances of 3.140(1) [Pd(1)] and 3.081(1) Å [Pd(2)] and tethered, by N–H···Br hydrogen bonds (H···Br distances of between 2.59 and 2.64 Å, N–H···Br angles between 163 and 172°); there is only one short C–H···Br contact with H···Br 2.84 Å and C–H···Br 171°. The absence of more C–H···Br interactions is probably a consequence of the phenyl rings in question entering into mutual π–π stacking (mean interplanar separation 3.52 Å) rather than directing their *ortho* hydrogen atoms towards the bromide centre (Fig. 3).

There are out-of-plane deviations of 0.47 [Pd(1)] and 0.49 Å [Pd(2)] of the metal centres out of their coordination planes in the direction of the encapsulated bromide anion. The upper and lower PdP_2S_2 units are again almost perfectly staggered, being rotated by 46° with respect to each other. The palladium and nickel coordination distances do not differ significantly from those seen in **1** (Table 1). As in **1**, there are stacking interactions between a diametrically opposite pair of phenyl rings and their proximal atu units (shortest atom···atom

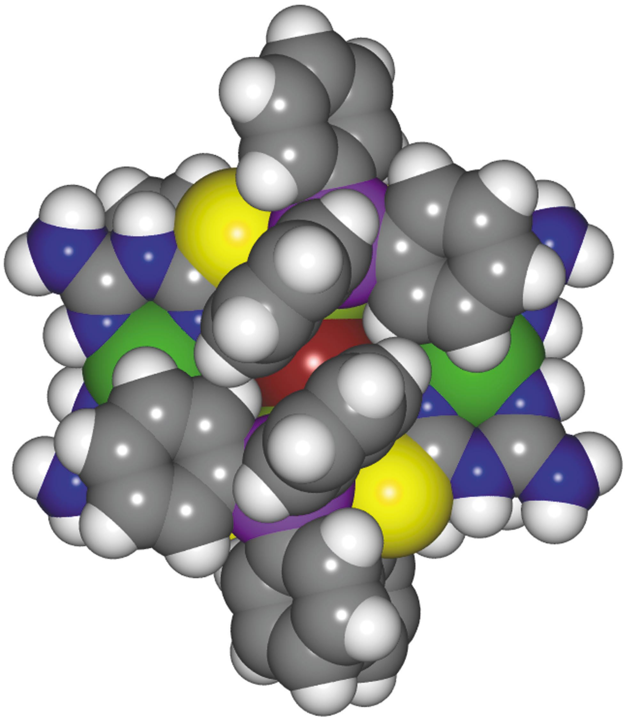


Fig. 3 Space-filling representation of **2** showing the π–π stacking of pairs of phenyl rings (centre of the figure) that effectively block the portals to the anion binding site (here occupied by a bromide ion coloured red/brown). The surrounding nickel and palladium centres are coloured green, the nitrogen atoms blue, the phosphorus centres violet, and the sulfur atoms (which are clearly exposed on the surface of the molecule) yellow.

contacts 3.13 and 3.32 Å). The oxygen atoms of the disordered perchlorate anions lie within hydrogen bonding distances of the outwardly directed atu N–H groups. There are no noteworthy intercomplex interactions.

Anion-directed synthesis of $[Pd_2Ni_2(atu)_4(PPh_3)_4I](ClO_4)_3$ 5

In order to further investigate the templating role of anions in the synthesis of these metalla-macrocycles, we decided to investigate the effect of iodide in the reaction between Pd-$(PPh_3)_2(CF_3SO_3)_2$ and $Ni(atu)_2$. In an analogous fashion to the chloride and bromide reactions described above, after $Pd(PPh_3)_2(CF_3SO_3)_2$ and $Ni(atu)_2$ had been reacting for two hours (and the $^{31}P\{^1H\}$ NMR spectrum of the reaction mixture showed only the AB pattern corresponding to **4**), stoichiometric amounts of iodide were added. Minutes after this anion was added, the $^{31}P\{^1H\}$ NMR spectrum of the mixture showed the appearance of a singlet at δ 18.5 ppm. The reaction mixture was left stirring for two hours after which time full conversion was observed. An orange solid was obtained after removal of the solvent under reduced pressure. This solid was washed with diethyl ether and recrystallised from methanol–diethyl ether. On the basis of $^{31}P\{^1H\}$ NMR, IR spectroscopy and elemental analyses, this product was characterised as the metalla-macrocycle $[Pd_2Ni_2(atu)_4(PPh_3)_4I](ClO_4)_3$ **5** demonstrating that iodide is also an effective templating agent for this reaction.

These experiments have clearly demonstrated that chloride, bromide and iodide are good templating agents for the synthesis of the metalla-macrocycles **1**, **2** and **5** (see Scheme 3), whereas bigger (and non-spherical) anions such as $CF_3SO_3^-$ and NO_3^- do not template their formation. The templating role of the smaller fluoride anion was also investigated but our results were inconclusive and further investigations will be required.

Solution studies on anion exchange

When equimolar amounts of the three metalla-macrocycles **1**, **2** and **5** were simultaneously dissolved in methanol, $^{31}P\{^1H\}$ NMR spectroscopy showed three sharp resonances at the characteristic chemical shifts for these compounds (*i.e.* at δ 22.0, 20.6 and 18.5 respectively). In order to study any potential exchange reactions between free halides and the metalla-macrocycles, several experiments were carried out. Upon addition of one equivalent of LiBr to a solution of **1**, full conversion to the bromide macrocycle **2** was observed by $^{31}P\{^1H\}$ NMR spectroscopy. However, the reverse reaction (*i.e.* addition of one equivalent of chloride to **2**) did not yield the chloride-containing macrocycle **1**. Similarly, the iodide-containing macrocycle was reacted with one equivalent of LiBr. In this case a singlet corresponding to **2** appeared even though the singlet for **5** was still present (in a 1 : 6 ratio). Addition of one equivalent of LiI to **2** did not produce the iodide-containing macrocycle **5**. These results indicate that in solution in the presence of extra halides the metalla-macrocycles undergo exchange reactions. These preliminary semi-quantitative results suggest that the bromide-containing macrocycle is the most stable of the three.

As can be seen from Fig. 3 the passage to the anion binding site is blocked by pairs of PPh_3 phenyl rings and significant conformational changes must take place for anion exchange to occur. At room temperature the energy required for these conformational changes to occur is obviously present. We are currently exploring the possibility of completely removing the halides from these metalla-macrocycles to enable a thorough study of the thermodynamic and kinetic aspects of the host–guest interactions.

Conclusion

The new metalla-macrocycles $[Pd_2Ni_2(atu)_4(PPh_3)_4X]^{3+}$ (X = Cl, Br, I) have been prepared using anion templated syntheses. Only in the presence of each of these three halides are the metalla-macrocycles formed. In the presence of larger anions such as triflate and nitrate, formation of only monometallic species is observed. These latter species can then be converted to the corresponding metalla-macrocycles by addition of the appropriate halide. An interesting feature of these metalla-macrocycles is that their encapsulated anions are mobile and can be interchanged in solution. Both solution and solid state experiments suggest that the bromide-containing macrocycle is the most stable. Experiments to completely remove the anions from the centre of the metalla-macrocycles are currently underway. These experiments should provide the *missing* species to permit a full kinetic and thermodynamic study of the host–guest interactions between the metalla-macrocycles and anions.

As stated in the Introduction, the role of anions as templating agents has only recently begun to be studied more extensively. We believe that the metalla-macrocycles described in this paper provide a unique system to help broaden our understanding of the templating capabilities of anions.

Experimental

General

Reactions were carried out routinely using Schlenk-line techniques under an atmosphere of pure nitrogen. The solvents were used dry and free of oxygen. IR spectra were recorded on a Perkin-Elmer 1720 Fourier-transform spectrometer between 4000 and 250 cm^{-1} as KBr pellets. $^{31}P\{^1H\}$ NMR spectra were performed on a JEOL JNM-EX270 Fourier-transform spectrometer operating at a frequency of 109.4 MHz with chemical shifts reported relative to H_3PO_4. Mass spectra were recorded by J. Barton at Imperial College on a VG AutoApec-Q as FAB using 3-nitrobenzyl alcohol as matrix. The compounds $Ni(atu)_2$,[18] $Pd(PPh_3)_2Cl_2$, $Pd(PPh_3)_2Br_2$

and $Pd(PPh_3)(CF_3SO_3)_2$ were prepared according to reported procedures.[19]

Syntheses

$[Pd_2(PPh_3)_4Ni_2(atu)_4Cl][ClO_4]_2Cl$ 1. To a solution of $Ni(ClO_4)_2{\cdot}6H_2O$ (0.15 g, 0.41 mmol) in methanol (20 ml), Hatu (0.09 g, 0.76 mmol) in methanol (25 ml) was added. An immediate colour change to dark orange-red [due to the formation of $Ni(atu)_2$] was observed. The resulting mixture was added to $PdCl_2(PPh_3)_2$ (0.29 g, 0.41 mmol) suspended in $CHCl_3$ (30 ml). The reaction mixture was left stirring at room temperature for two hours. The solvent was evaporated under reduced pressure and the resulting orange solid was recrystallised from a methanol–diethyl ether mixture. Yield 0.23 g (54%). Found: C, 45.51; H, 3.64; N, 10.74. $C_{80}H_{80}N_{16}P_4S_4O_8Cl_4Ni_2Pd_2$ requires C, 45.41; H, 3.78; N, 10.60%. ν_{max}/cm^{-1} (KBr) 3345s, 3195s (NH), 3052m (CH), 1664s, 1596s (CN), 1481m (Ph), 1093s (ClO_4^-). δ_P (MeOH) 22.0 (s).

$[Pd_2(PPh_3)_4Ni_2(atu)_4Br][ClO_4]_2Br$ 2. To a solution of $Ni(ClO_4)_2{\cdot}6H_2O$ (0.03 g, 0.09 mmol) in methanol (10 ml), Hatu (0.02 g, 0.17 mmol) in methanol (15 ml) was added. An immediate colour change to dark orange [due to the formation of $Ni(atu)_2$] was observed. The resulting mixture was added to $PdBr_2(PPh_3)_2$ (0.07 g, 0.09 mmol) suspended in CH_3CN (20 ml). The reaction mixture was left stirring at room temperature for two hours. The solvent was evaporated under reduced pressure and the resulting orange solid was recrystallised from methanol–diethyl ether. Yield 0.07 g (74%). Found: C, 43.30; H, 3.65; N, 10.14. $C_{80}H_{80}N_{16}P_4S_4O_8Br_2Cl_2Ni_2Pd_2$ requires C, 43.56; H, 3.63; N, 10.16%. ν_{max}/cm^{-1} (KBr) 3364s, 3200s (NH), 3054m (CH), 1658s, 1599s (CN), 1480m (Ph), 1090s (ClO_4^-). δ_P (MeOH) 20.6 (s).

Synthesis of $[Pd(PPh_3)_2(atu)][CF_3SO_3]_2$ 4 from Hatu and $Pd(PPh_3)_2(CF_3SO_3)_2$. A solution of Hatu (0.05 g, 0.46 mmol) in methanol (25 ml) was added to a solution of $Pd(PPh_3)_2(CF_3SO_3)_2$ (0.43 g, 0.46 mmol) in THF (20 ml). The reaction mixture was left stirring at room temperature for two hours. Most of the solvent was evaporated under reduced pressure and a yellow solid precipitated upon addition of diethyl ether. Yield: 0.29 g (60%). Found: C, 45.76; H, 3.37; N, 5.24. $C_{40}H_{36}N_4P_2S_3O_6F_6Pd$ requires C, 45.89; H, 3.44; N, 5.35%. ν_{max}/cm^{-1} (KBr) 3330s, 3200s (NH), 3061m (CH), 1686m, 1585m (CN), 1481m (Ph), 1260s ($CF_3SO_3^-$). δ_P (MeOH) 32.4 (d, J = 25 Hz, 1P), 30.5 (d, J = 25 Hz, 1P). FAB-MS$^+$: m/z 747 {$[Pd(PPh_3)_2(atu)]^+$}, 630 {$[Pd(PPh_3)_2]^+$}, 485 {$[Pd(PPh_3)(atu)]^+$}.

Synthesis of 1 from $Pd(PPh_3)_2(CF_3SO_3)_2$. To a solution of $Ni(ClO_4)_2{\cdot}6H_2O$ (0.08 g, 0.22 mmol) in methanol (15 ml), Hatu (0.05 g, 0.44 mmol) in methanol (25 ml) was added. An immediate colour change to dark orange [due to the formation of $Ni(atu)_2$] was observed. The resulting mixture was added to a solution of $Pd(PPh_3)_2(CF_3SO_3)_2$ (0.20 g, 0.22 mmol) in THF (30 ml). A few minutes later LiCl (0.01 g, 0.22 mmol) was added as a solid to the reaction mixture which was left stirring at room temperature for two hours. The solvent was evaporated under reduced pressure and the resulting orange solid was recrystallised from methanol–diethyl ether. Yield 0.18 g (73%). Found: C, 44.89; H, 3.80; N, 9.94. $C_{81}H_{80}N_{16}P_4S_5O_{11}Cl_3F_3Ni_2Pd_2{\cdot}THF$ requires C, 44.35; H, 3.83; N, 9.74%. ν_{max}/cm^{-1} (KBr) 3354s, 3205s (NH), 3054m (CH), 1666s, 1602s (CN), 1481m (Ph), 1257s ($CF_3SO_3^-$). δ_P (MeOH) 22.1 (s).

Synthesis of 2 from $Pd(PPh_3)_2(CF_3SO_3)_2$. To a solution of $Ni(ClO_4)_2{\cdot}6H_2O$ (0.12 g, 0.32 mmol) in methanol (15 ml), Hatu (0.07 g, 0.64 mmol) in methanol (30 ml) was added. An immediate colour change to dark orange [due to the formation of $Ni(atu)_2$] was observed. The resulting mixture was added to a solution of $Pd(PPh_3)_2(CF_3SO_3)_2$ (0.30 g, 0.32 mmol) in THF (30 ml). A few minutes later LiBr (0.01 g, 0.16 mmol) was added as a solid to the reaction mixture which was left stirring at room temperature for two hours. The solvent was evaporated under reduced pressure and the resulting orange solid was recrystallised from methanol–diethyl ether. Yield 0.11 g (30%). Found: C, 43.25; H, 3.49; N, 10.17. $C_{80}H_{80}N_{16}P_4S_4O_{12}BrCl_3Ni_2Pd_2$ requires C, 43.20; H, 3.60; N, 10.07%. ν_{max}/cm^{-1} (KBr) 3359s, 3205s (NH), 3053m (CH), 1664s, 1600s (CN), 1481m (Ph), 1094 (ClO_4^-). δ_P (MeOH) 20.4 (s).

Synthesis of $[Pd_2(PPh_3)_4Ni_2(atu)_4I][ClO_4]_3$ 5 from $Pd(PPh_3)_2(CF_3SO_3)_2$. To a solution of $Ni(ClO_4)_2{\cdot}6H_2O$ (0.08 g, 0.22 mmol) in methanol (15 ml), Hatu (0.05 g, 0.44 mmol) in methanol (25 ml) was added. An immediate colour change to dark orange [due to the formation of $Ni(atu)_2$] was observed. The resulting mixture was added to a solution of $Pd(PPh_3)_2(CF_3SO_3)_2$ (0.20 g, 0.22 mmol) in THF (30 ml). A few minutes later KI (0.02 g, 0.11 mmol) was added as a solid to the reaction mixture which was left stirring at room temperature for two hours. The solvent was evaporated under reduced pressure and the resulting dark orange solid was recrystallised from methanol–diethyl ether. Yield 0.20 g (80%). Found: C, 42.21; H, 3.43; N, 9.92. $C_{80}H_{80}N_{16}P_4S_4O_{12}ICl_3Ni_2Pd_2$ requires C, 42.29; H, 3.52; N, 9.87%. ν_{max}/cm^{-1} (KBr) 3343s, 3214s (NH), 3053m (CH), 1663s, 1599s (CN), 1481m (Ph), 1092s (ClO_4^-). δ_P (MeOH) 18.5 (s).

Crystallography

Crystal data for 1. $[C_{80}H_{80}N_{16}P_4S_4Ni_2Pd_2{\cdot}Cl][ClO_4]_3{\cdot}3EtOH$, $M = 2319.9$, monoclinic, space group $C2/c$ (no. 15), $a = 19.601(2)$, $b = 36.841(3)$, $c = 18.233(2)$ Å, $\beta = 118.74(1)°$, $V = 11544(2)$ Å^3, $Z = 4$ (C_2 symmetry), $D_C = 1.335$ g cm^{-3}, μ(Cu-Kα) = 5.39 mm^{-1}, $T = 183$ K, orange prisms; 8500 independent measured reflections, F^2 refinement, $R_1 = 0.079$, $wR_2 = 0.198$, 5770 independent observed absorption corrected reflections [$|F_o| > 4\sigma(|F_o|)$, $2\theta < 120°$], 620 parameters.

Crystal data for 2. $[C_{80}H_{80}N_{16}P_4S_4Ni_2Pd_2{\cdot}Br][ClO_4]_{2.5}[Br]_{0.5}{\cdot}7EtOH$, $M = 2538.9$, triclinic, space group $P\bar{1}$ (no. 2), $a = 13.021(3)$, $b = 13.941(2)$, $c = 31.507(5)$ Å, $\alpha = 101.34(2)$, $\beta = 98.82(1)$, $\gamma = 92.44(1)°$, $V = 5526(2)$ Å^3, $Z = 2$, $D_C = 1.526$ g cm^{-3}, μ(Cu-Kα) = 5.98 mm^{-1}, $T = 193$ K, yellow prismatic needles; 14702 independent measured reflections, F^2 refinement, $R_1 = 0.082$, $wR_2 = 0.215$, 10444 independent observed absorption corrected reflections [$|F_o| > 4\sigma(|F_o|)$, $2\theta < 114°$], 1177 parameters.

CCDC reference numbers 162411 and 162412.

See http://www.rsc.org/suppdata/dt/b1/b102633j/ for crystallographic data in CIF or other electronic format.

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