Chapter 5: Cyclophanes incorporating imidazole-2-thione

5.1 Introduction

The Baker group has been interested in imidazolium-linked cyclophanes such as \(30 \cdot 2HX\), \(32 \cdot 2HX\) and \(77 \cdot 2HX\), and has studied their interesting conformational behaviour using X-ray diffraction and NMR methods.\(^1-^3\) While a great many imidazole-2-thiones are known,\(^4-^{13}\) including examples where IMT moieties are appendages to a calixarene.\(^{14}\) There have been no reports of cyclophane structures analogous to \(30 \cdot 2HX\), \(32 \cdot 2HX\) and \(77 \cdot 2HX\) in which IMT moieties are part of a macrocyclic ring. The present study will explore the synthesis of some cyclophanes incorporating IMT units, and characterisation of their conformational behaviour in the solid state and in solution.

\[\text{30} \cdot 2HX, \quad \text{32} \cdot 2HX, \quad \text{77} \cdot 2HX\]
5.2 Synthesis of the imidazole-2-thiones

The imidazole-2-thiones 31 and 33, or 78-81 were synthesized by reaction of the corresponding imidazolium salts with sulfur and K$_2$CO$_3$ in methanol at 40 °C overnight. In most cases the products were sufficiently pure for further use, but in some cases recrystallisation was required to obtain analytically pure samples. The conformations of the cyclophanes 31, 33 and 81 were investigated using X-ray diffraction and NMR studies.
5.3 **Structures and conformations of imidazol-2-thione cyclophanes**

Crystals of 31 and 33 were grown by slow evaporation of their solutions in CH$_2$Cl$_2$, while crystals of 81 were grown by slow evaporation of a solution of the compound in 1:1 CH$_2$Cl$_2$ / ethyl acetate. Results of X-ray diffraction studies are summarized in Table 5.1 and Figures 5.1-3.

**Table 5.1** Crystal data of 31, 33 and 81.

<table>
<thead>
<tr>
<th>Complex</th>
<th>31</th>
<th>33</th>
<th>81</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Empirical formula</strong></td>
<td>C$<em>{22}$H$</em>{20}$N$_4$S$_2$</td>
<td>C$<em>{22}$H$</em>{20}$N$_4$S$_2$</td>
<td>C$<em>{28}$H$</em>{22}$N$_4$S$_2$</td>
</tr>
<tr>
<td><strong>Formula weight</strong></td>
<td>404.54</td>
<td>404.54</td>
<td>488.69</td>
</tr>
<tr>
<td><strong>Wavelength / Å</strong></td>
<td>0.71073</td>
<td>1.54184</td>
<td>1.54178</td>
</tr>
<tr>
<td><strong>Crystal system</strong></td>
<td>Monoclinic</td>
<td>Monoclinic</td>
<td>Orthorhombic</td>
</tr>
<tr>
<td><strong>Space group</strong></td>
<td>P2$_1$/n</td>
<td>P2$_1$/c</td>
<td>Pbcm</td>
</tr>
<tr>
<td><strong>a / Å</strong></td>
<td>17.7030(7)</td>
<td>16.5418(17)</td>
<td>11.4440(2)</td>
</tr>
<tr>
<td><strong>b / Å</strong></td>
<td>10.5275(4)</td>
<td>9.4045(7)</td>
<td>12.3977(2)</td>
</tr>
<tr>
<td><strong>c / Å</strong></td>
<td>20.7005(8)</td>
<td>12.7453(13)</td>
<td>17.1168(2)</td>
</tr>
<tr>
<td><strong>β /°</strong></td>
<td>99.500(4)</td>
<td>102.919(10)</td>
<td>-</td>
</tr>
<tr>
<td><strong>V/ Å$^3$</strong></td>
<td>3805.0(3)</td>
<td>1932.6(3)</td>
<td>2428.52(6)</td>
</tr>
<tr>
<td><strong>Z</strong></td>
<td>8</td>
<td>4</td>
<td>4</td>
</tr>
<tr>
<td><strong>ρ(calc)/Mg m$^{-3}$</strong></td>
<td>1.412</td>
<td>1.390</td>
<td>1.337</td>
</tr>
<tr>
<td><strong>μ/ mm$^{-1}$</strong></td>
<td>0.296</td>
<td>2.613</td>
<td>2.17</td>
</tr>
<tr>
<td><strong>Crystal size/ mm$^3$</strong></td>
<td>0.207 x 0.168 x 0.085</td>
<td>0.119 x 0.082 x 0.017</td>
<td>0.282 x 0.164 x 0.025</td>
</tr>
<tr>
<td><strong>θ range for data collection/°</strong></td>
<td>2.18 to 28.28</td>
<td>2.74 to 67.49</td>
<td>3.86 to 67.32</td>
</tr>
<tr>
<td><strong>Reflections collected</strong></td>
<td>14977</td>
<td>9530</td>
<td>19862</td>
</tr>
<tr>
<td><strong>Independent reflections</strong></td>
<td>8394</td>
<td>3435</td>
<td>2266</td>
</tr>
</tbody>
</table>
The o-cyclophane 31 adopts a conformation reminiscent on the cone conformation of calix[4]arenes, with the benzene and IMT rings forming a "cup" and the C=S groups being oriented exo relative to the macrocyclic ring. The IMT rings are approximately parallel, so the cup is somewhat flattened. The C=S bonds are bent slightly out of the N2C2 planes of the imidazole-2-thiones, presumably as a consequence of steric repulsion between the S atoms. The molecules form pairs with their cups interlocked (Figure 1b), the pairs then stacking into columns seemingly in response to interactions between benzene rings (intermolecular distance between C6 planes ~3.377 Å).
Figure 5.1 Crystal structure (50% probability level for the displacement ellipsoids) of 31, showing (a) a single molecule; (b) an interlocked pair; and (c) a column of interlocked pairs. Selected bond lengths (Å) and angles (°): S(22)-C(22) 1.680(3), S(62)-C(62) 1.678(3), C(1)-N(21) 1.472(4), C(1)-C(11) 1.516(4), C(2)-N(23) 1.477(4), C(4)-C(12) 1.514(4), C(2)-C(32) 1.524(4), C(3)-C(31) 1.517(4), N(41)-C(42)-S(24) 127.1(2), N(43)-C(42)-S(42) 127.8(2).
The mesitylene-derived \textit{m}-cyclophane 81 also adopts a conformation reminiscent of cone conformation of calix[4]arenes. In this case, however, the IMT rings are splayed apart so that the S atoms avoid unfavourable steric interactions with C2 methyl substituent on each of the benzene rings, and that the "cup" is now quite pinched. Evidently the geometry of the \textit{m}-cyclophane skeleton permits the splaying apart of the thione rings, so that the C=S bond is not bent out of the C$_3$N$_2$ plane (\textit{cf.} the case for the \textit{o}-cyclophane 31). The conformation seen for 81 contrasts with the 1,3-alternate-type conformation seen for the parent imidazolium-linked cyclophane 77·2HBr,$^{15}$ in which the imidazolium groups are oriented with the C2-H bond directed into the cavity formed between the mesitylene groups. It may be that the corresponding orientation for the imidazole thione groups in 81 is disfavoured by electronic repulsion between the electron-rich C=S groups.

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{image.png}
\caption{Crystal structure (50\% probability level for the displacement ellipsoids) of 81. Selected bond lengths (Å) and angles (°): S(1)-C(22) 1.693(2), C(1)-N(21) 1.465(3), C(1)-C(12) 1.513(3), C(2)-N(23) 1.474(3), C(2)-C(36) 1.532(3), N(21)-C(1)-C(12) 110.82(17), N(23)-C(2)-C(36) 109.40(17). Only one set of the disordered hydrogen atoms has been shown.}
\end{figure}
In contrast to 31 and 81, the \( m \)-cyclophane 33 adopts an \textit{anti} conformation reminiscent of the 1,2-alternate conformation of calix[4]arene (Figure 5.3). There are two distinct molecules in the unit cell, each with their \( m \)-xyylene groups approximately parallel. The imidazole thione groups also parallel, but oriented approximately orthogonal to the \( m \)-xyylene groups, and with their C=S groups pointing in opposite directions. There is some disorder in orientation of one of the imidazole thione groups in one of the molecules, so that some of 33 is present in a partial cone conformation as a minor component of molecule 2.
Figure 5.3 Crystal structure (20% probability level for the displacement ellipsoids) of the two distinct molecules of 33. Left, molecule 1. Right, the major component of molecule 2. Selected bond lengths (Å) and angles (°): S(22)-C(22) 1.686(6), S(52)-C(52) 1.67(1), C(1)-N(21) 1.462(7), C(1)-C(11) 1.515(8), C(2)-N(23) 1.436(7), C(4)-C(33) 1.598(18), C(2)-C(13') 1.517(8), C(3)-C(31) 1.497(9), N(23)-C(22)-S(22) 126.2(5), N(21)-C(22)-S(22) 128.3(4), N(53)-C(52)-S(52) 123.8(7), N(51)-C(52)-S(52) 127.7(8) where the prime refers to the atom generated by the crystallographic inversion centre.
NMR spectra (DMSO-\textit{d}_6 solution, room temperature) of the IMT ligands showed signals expected for the proposed structures (Table 5.2). The number and splitting patterns of the signals seen in the $^1$H NMR spectrum of $81$ are consistent with the cone conformation seen in the solid state being maintained in solution. The sharpness of the signals indicates that interconversion between the two equivalent (mirror image) forms of this conformation does not occur on the NMR timescale. Similar conformational rigidity has been reported previously\(^\text{15}\) for the precursor imidazolium-linked cyclophane $77\cdot2\text{HBr}$ ($^1$H NMR spectrum included for comparison in Figure 5.4). The $^1$H NMR chemical shift of the protons on the IMT group in $81$ is markedly upfield ($\delta$ 5.63 ppm, compared with $\delta$ 7.11 and 7.14 ppm seen for the corresponding protons in $80$). This upfield shift is consistent with the protons of the IMT groups being in a region where they experience shielding by the ring currents of the benzene rings,\(^\text{15}\) and thus provides additional evidence that the conformation in solution is similar to that seen in the solid state. In the imidazolium cyclophane $77\cdot2\text{HBr}$, the imidazole H4/H5 protons appear far downfield ($\delta$ 8.02 ppm), in part due to the positive charge associated with the imidazolium rings, but also due to cyclophane existing in the 1,3-alternate type conformation, which places the imidazolium H4/H5 protons far from the shielding effects of the benzene rings.\(^\text{15}\)
Figure 5.4 Downfield region of the $^1$H NMR spectra (600 MHz, DMSO-$d_6$) for solutions of (a) the ligand 81 (b) its precursor imidazolium-linked cyclophane 77·2HBr.

The $^1$H NMR spectrum of 31 in DMSO-$d_6$ solution at room temperature (Figure 5.5) is also consistent with the cyclophane macrocycle adopting a cone-type conformation in solution, as seen in the solid state. Again, the IMT H4/H5 protons have a significantly upfield chemical shift (~5.70 ppm), indicative of these protons being shielded by the ring currents of the benzene rings. Interestingly, while the pair of sharp doublets seen for the benzylic protons (exo and endo environments) indicates that the cone conformation of 31 is rigid on the NMR timescale, the $^1$H NMR spectrum of the parent imidazolium cyclophane 30·2HBr shows broadened signals, a consequence of rapid interconversion of several conformations in solution$^{15}$ (Figure 5.5). Presumably
the increased bulkiness of the thione groups in 31 compared to the imidazolium groups in 30.2HBr decreases the conformational lability of its cyclophane structure.

Figure 5.5 Downfield region of the $^1$H NMR spectra (600 MHz, DMSO-$d_6$) for solutions of (a) the ligand 31 (b) its precursor imidazolium-linked cyclophane 30·2HBr.

For 33, the situation is more complicated. The $^1$H NMR spectrum in DMSO-$d_6$ solution contains two sets of signals with integrals in a ratio of 2.3 : 1 (Figure 5.6). These signals can be attributed to two distinct conformations differ in the orientation of the two IMT groups—in one, these groups are aligned mutually syn, in the other these groups are aligned mutually anti (Figure 5.7). Each conformation showed one pair of doublets for the benzylic methylene protons, indicating that the IMT units do not rotate about their N—N axes on the NMR timescale, and variable temperature studies showed
that these conformations do not interconvert on the NMR timescale even at 80 °C. This result implies that the cyclophane macrocycle is too small to allow passage of either the C=S moiety of the C_2H_2 moiety of the IMT unit. This result contrasts with the case for the parent imidazolium meta-cyclophane 32·2HBr, which is conformationally labile.\textsuperscript{15}

**Figure 5.6** Downfield region of the $^1$H NMR spectra (600 MHz, DMSO-$d_6$) for solutions of (a) the ligand 33 and (b) its precursor imidazolium-linked cyclophane 32·2HBr.

The chemical shifts of the various proton environments in the two conformations are similar, so it is not possible to assign a particular conformation to a particular set of NMR signals. Interestingly, the similarity of the NMR signals suggests that there is no
significant difference in shielding due to, for example, the ring currents associated with the arene rings. This observation is consistent with the arene rings being oriented with their planes nearly parallel to the N—N axes of the IMT groups (as seen in the solid state), so that regions of shielding are far removed from the environments of the benzylic and imidazole H4/H5 protons. For the *anti* conformation, if the arene rings are approximately parallel (as seen in the solid state), the methylene groups would not be strictly equivalent, but would be rendered equivalent by slight rocking of the arene rings (Figure 5.7). Similar considerations apply to the *syn* conformation.

![Diagram of syn and anti conformations](image)

Figure 5.7 The *syn* and *anti* conformations of 33, and rocking of the arene rings in the *anti* conformation that would make the methylene groups equivalent.
Table 5.2 $^1$H NMR data$^a$ for imidazole-2-thiones

<table>
<thead>
<tr>
<th>Compound</th>
<th>CH$_3$</th>
<th>CH$_2$</th>
<th>H4/H5</th>
<th>Aromatics</th>
</tr>
</thead>
<tbody>
<tr>
<td>31$^b$</td>
<td>-</td>
<td>4.55 (4H, d, $^2$J$_{H,H}$ 14.5 Hz)</td>
<td>5.70 (4H, s)</td>
<td>7.63-7.62, 7.51-7.49</td>
</tr>
<tr>
<td></td>
<td></td>
<td>5.71 (4H, d, $^2$J$_{H,H}$ 14.5 Hz)</td>
<td></td>
<td>(8H, AX pattern)</td>
</tr>
<tr>
<td>33$^c$</td>
<td>-</td>
<td>4.90 (4H, d, $^2$J$_{H,H}$ 16 Hz)</td>
<td>6.93 (2H, s)</td>
<td>7.39 (3H, m)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>5.74 (2H, d, $^2$J$_{H,H}$ 16 Hz)</td>
<td></td>
<td>7.32-7.29 (6H, m)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>4.86 (2H, d, $^2$J$_{H,H}$ 16 Hz)</td>
<td></td>
<td>6.33 (2H, s)</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>6.23 (1H, s)</td>
</tr>
<tr>
<td>78</td>
<td>3.55 (6H, s)</td>
<td>-</td>
<td>6.99 (2H, s)</td>
<td>-</td>
</tr>
<tr>
<td>79</td>
<td>3.51 (6H, s)</td>
<td>5.30 (4H, s)</td>
<td>7.20 (2H, d, $^3$J$_{H,H}$ 2.5 Hz)</td>
<td>7.27-7.25, 6.96-6.94</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>7.02 (2H, d, $^3$J$_{H,H}$ 2.5 Hz)</td>
</tr>
<tr>
<td>Compound</td>
<td>CH₃</td>
<td>CH₂</td>
<td>H4/H5</td>
<td>Aromatics</td>
</tr>
<tr>
<td>----------</td>
<td>-----------</td>
<td>----------------</td>
<td>----------------------------------------</td>
<td>--------------------</td>
</tr>
<tr>
<td>80</td>
<td>3.48 (6H, s)</td>
<td>5.17 (4H, s)</td>
<td>7.14 (2H, d, 3Jₜ,ₜ 2.5 Hz)</td>
<td>7.30 (1H, s)</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>7.11 (2H, d, 3Jₜ,ₜ 2.5 Hz)</td>
<td>7.28 (1H, t, 3Jₜ,ₜ 4 Hz)</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>7.16 (2H, d, 3Jₜ,ₜ 4 Hz)</td>
<td></td>
</tr>
<tr>
<td>81ᵇ</td>
<td>2.39 (12H, s)</td>
<td>5.52 (4H, d, 2Jₜ,ₜ 14.4 Hz)</td>
<td>5.63 (4H, s)</td>
<td>6.98 (2H, s)</td>
</tr>
<tr>
<td></td>
<td>1.56 (6H, s)</td>
<td>4.70 (4H, d, 2Jₜ,ₜ 14.4 Hz)</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

ᵃ Recorded at 500.10 MHz and ambient temperature from solutions in DMSO-d₆.
ᵇ Recorded at 600.13 MHz and ambient temperature from solutions in DMSO-d₆.
ᶜ Chemical shift listed in normal type involve anti conformation, chemical shift listed in italics type involve syn conformation, chemical shift listed in **bold** type overlapping signals between both conformations.
5.4 References


Chapter 6: Au\textsuperscript{I} complexes of imidazole-2-thiones

6.1 Introduction

As mentioned in Chapter 2, aurophilic Au···Au interactions have been one of the most interesting topics in gold chemistry, and have been the subject of significant studies in the physical and chemical properties of gold compounds.\textsuperscript{1-4} Au\textsuperscript{I} complexes have been studied with their photophysical properties, which are sometimes due to intramolecular aurophilic interactions.\textsuperscript{5,6} The term "aurophilic interaction" was recognised by Schmidbaur in the early 1990s to be operative between linearly two-coordinate, closed shell Au\textsuperscript{I} centres (electronic configuration 5d\textsuperscript{10}).\textsuperscript{3,4} It has been shown that the luminescence properties exhibited by various dinuclear Au\textsuperscript{I}-phosphine and dinuclear Au\textsuperscript{I}-NHC complexes are significantly influenced by presence of aurophilic interactions.\textsuperscript{5-8}

Many complexes of Ag\textsuperscript{I}, \textsuperscript{9-12} Cu\textsuperscript{I}, \textsuperscript{11,13} Ni\textsuperscript{II}, \textsuperscript{14} Co\textsuperscript{II}, \textsuperscript{14} Zn\textsuperscript{II}, \textsuperscript{15} Pd\textsuperscript{II}, \textsuperscript{11} Ir\textsuperscript{I}, \textsuperscript{16-19} Rh\textsuperscript{I}, \textsuperscript{16-19} and Re\textsuperscript{I} \textsuperscript{20} with IMT ligands have been reported. There are, however, few examples of Au\textsuperscript{I} complexes of IMTs and closely related ligands.\textsuperscript{10,21,23} Yan \textit{et al.} prepared 18\textsuperscript{+} by the reaction of the corresponding \(N,N\)-disubstituted imidazolidine-2-thione with [Au(THT)Cl] (THT = tetrahydrothiophene) and examined its biological activities.\textsuperscript{22} Alvarado \textit{et al.} also reported the synthesis and catalytic activity of substituted Au\textsuperscript{I}-IMT complexes such as 19.\textsuperscript{23}
The ease of synthesis of IMTs and the high affinity of sulfur-donors for Au\(^{1}\) centres suggests that an investigation of reactions of IMTs with Au\(^{1}\) should readily yield a trove of interesting new chemistry. For example, using appropriate bis(IMT) ligands, it should be possible to engineer the formation of dinuclear Au\(^{1}\)-IMT complexes with strong intramolecular aurophilic interactions and interesting photophysical properties. This chapter reports the synthesis and structural characterisation of a series of new substituted Au\(^{1}\)-IMT (including mono-, di- and trinuclear Au\(^{1}\)-IMT complexes) and studies of their photophysical and electrochemical properties.

### 6.2 Synthesis of Au\(^{1}\)-IMT complexes

The Au\(^{1}\)-IMT complexes \(85\cdot\text{Cl} - 90\cdot\text{Cl}, 91, 92\cdot\text{Cl}\) and \(93\cdot\text{Cl}\) were synthesized in yields of 42-91% by direct metalation of the corresponding IMT ligands \(78 - 84\) and \(31, 33\) with a suitable Au\(^{1}\) precursor \([\text{Au(SMe}_2]\text{Cl}]\) in dichloromethane at room temperature overnight. In most of the cases, Au\(^{1}\) complex was obtained cleanly, and the Au\(^{1}\) centre was bound to two IMT groups via S (see X-ray studies, below). In the case of ligand \(33\),
two products were formed—an adduct of 33 with two AuCl units, 91, and the Au\textsuperscript{I}-bis(IMT) complex 92·Cl. These two complexes presumably arise via reactions of Au\textsuperscript{I} with the anti and syn conformations of 33 respectively.
The synthesis of Au^I^ complexes incorporating the o-cyclophane bis(thione) 31 was attempted according to the same conditions used with the other IMT ligands. However, when 31 was added to a solution of [Au(SMe)_2]Cl in dichloromethane at room temperature, the mixture immediately became dark blue, suggesting that gold colloids were formed. The experiment was repeated several times with slight variations, but even at 0 °C the result was the same. When a reaction mixture was filtered (to separate most of the colloidal gold) and the filtrate stripped of solvent under vacuum, a pale blue solid was obtained. This solid was characterized by ^1^H NMR spectroscopy and mass spectrometry. The ESI mass spectra obtained from acetonitrile solutions of the product contained two molecular ion clusters. The major molecular ion occurred near m/z = 1005.1298, with associated isotopomers appearing at m/z near 1006, 1007, 1008 and 1009, and these masses suggest a product such as 94^+^ (m/z calc'd = 1005.1924). The minor molecular ion appeared as a weak signal near m/z = 601.0759, suggesting a
structure such as 95$^+$(m/z calc'd = 601.0795). The $^1$H NMR spectrum of the product in DMSO-$d_6$ solution showed similar signals as seen for 31, but broader and at slightly different chemical shifts (more downfield). The signals due to the benzylic protons were particularly broad, suggesting some conformational lability. Two distinct signals were seen for imidazolyl H4/H5 protons, consistent with the presence of two distinct imidazole-2-thione environments, as in 94$^+$. No evidence for a discrete species 95$^+$ was seen in the $^1$H NMR spectrum. Unfortunately, numerous attempts to crystallise an Au$^+$-IMT complex from the product mixtures gave only crystals if 31.

\[ \text{94}^+ \quad \text{95}^+ \]

With the exception of 87·Cl, the Au$^+$ IMT complexes are soluble in polar organic solvents (e.g., DMSO, methanol, CH$_3$CN, acetone) but poorly soluble in non-polar organic solvents (ether, hexanes). The complex 87·Cl was only sparingly soluble in DMSO but poorly soluble in other solvents. All of the complexes are stable in the solid state for extended periods. In DMSO solutions, however, the complexes slowly decompose and the solutions change from colourless to purple, suggestive of formation of colloidal Au.
Crystals suitable for X-ray diffraction studies were grown for 85·3Cl, 86·2Cl, 88·2Cl, 91 and 92·Cl. Suitable crystals could not be grown for 87·2Cl, 89·2Cl, 90·Cl, and so these salts were converted to their hexafluorophosphate analogues by metathesis with KPF₆ in aqueous methanol, and the complexes crystallised as hexafluorophosphate salts.

### 6.3 Single crystal X-ray diffraction studies

Crystals of 85·Cl(H₂O)₀.₆₇(CH₂Cl₂)₀.₆₇, 86·Cl, 87·2PF₆, 88·2Cl, 89·2PF₆, 90·(AuCl₂)₀.₂₀₃Cl₀.₂₆₀(PF₆)₀.₅₃₇(H₂O)₀.₁₃₀, 91', 91'', and 93·Cl(CH₃OH)(H₂O) were characterized by X-ray diffraction. Crystallographic data are summarized in Tables 6.1 and 6.2. For each bis(IMT) complex, the IMT ligands provide an essentially linear coordination array around the Au⁺ centres (S-Au-S 169.98(5)-179.34(17)°; Au—S 2.225(18)-2.432(11) Å), with the IMT C=S bonds roughly orthogonal to the S-Au-S axis (C-S-Au 93.7(4)-108.2(10)°). These characteristics are in line with those of related Au⁺ complexes 18⁺ and 19 reported previously.²²,²³ Interesting features of individual structures are discussed below.

For 85·Cl(H₂O)₀.₆₇(CH₂Cl₂)₀.₆₇, the cations 85⁺ form linear trimers held together by aurophilic interactions (Au···Au 3.0466(1) Å, Au···Au···Au 180°), with the terminal S—Au—S axes orthogonal to the central one (Figure 6.1). Interestingly, the planes of the two IMT moieties associated with each Au centre are approximately parallel. In the central Au(IMT)₂ unit, the IMT moieties are oriented mutually *trans* about the central S-Au-S axis (dihedral angle of C=S groups 180°), and each heterocyclic ring is
positioned so that its centroid lies over one of the terminal Au atoms (Au···N$_2$C$_3$ 3.704 Å). In each of the terminal Au(IMT)$_2$ units, the IMT moieties take on a gauche-type arrangement about the central S-Au-S axis (dihedral angle of C=S groups 89.08°), one IMT group oriented so that the centroid of its heterocyclic ring lies over one of the S atoms of the central S-Au-S moiety (S···N$_2$C$_3$ 3.604 Å).

**Figure 6.1** Crystal structure (50% probability level for the displacement ellipsoids) of the trimeric cation of 85-3Cl(CH$_2$Cl)$_2$(H$_2$O)$_2$. Selected bond lengths (Å) and angles (°): Au(1)···S(1) 2.3178(9), Au(1)···S(1′) 2.3177(9), Au(2)···S(3) 2.2875(9), Au(2)···S(2) 2.2958(9), Au(1)···Au(2′) 3.0466(1), C(11)-S(1)-Au(1) 103.10(11), C(21)-S(2)-Au(2) 106.15(12), C(31)-S(3)-Au(2) 106.66(12), S(1′)-Au(1)-S(1) 180.0, S(3)-Au(2)-S(2) 172.46(3), Au(2′)-Au(1)-Au(2) 180.0, where the primes refer to the atom generated by the crystallographic inversion.
For 86·Cl, the cations are also involved in aurophilic interactions (Au···Au 3.0647(12) Å), but in this case (perhaps as a consequence of increased steric bulk of the IMT ligand compared to the case for 85\(^+\)) only dimers are formed (Figure 6.2). Again, the two IMT moieties associated with each Au centre are approximately parallel. The dimers are arranged into chains, each Au(IMT)\(_2\) unit being involved in two close Au···S contacts (Au···S ~ 3.48(1) Å, *cf*. sum of the van der Waals radii ~ 3.46 Å\(^{24}\)) with an Au(IMT)\(_2\) unit of an adjacent dimer.

**Figure 6.2** Crystal structure (50% probability level for the displacement ellipsoids) of the cation of 86·Cl. Selected bond lengths (Å) and angles (°): Au(1)···S(1) 2.225(18), Au(1)···S(4) 2.240(7), Au(1)···S(3) 2.323(15), Au(1)···S(2) 2.432(11), Au(1)···Au(1') 3.0647(12), S(1)-Au(1)-S(4) 160.5(4), S(4)-Au(1)-S(3) 172.5(5), S(1)-Au(1)-S(2) 175.8(5), S(3)-Au(1)-S(2) 164.2(6), C(11)-S(1)-Au(1) 104.5(13), C(21)-S(2)-Au(1) 108.2(10), C(31)-S(3)-Au(1) 103.7(11), C(41)-S(4)-Au(1) 100.6(8), where the prime refers to the atom generated by the crystallographic 2-fold axis.
For $87\cdot2\text{PF}_6$, the cation $87^{2+}$ is dinuclear, of form $\text{Au}_2\{\text{bis(IMT)}\}_2$, with an intramolecular aurophilic interaction ($\text{Au}\cdots\text{Au} \ 3.0505(3) \ \text{Å}$). One thione group from each ligand binds to each Au$^+$ centre, so that the ligands constitute a short spiral that forms a cup about the Au$\cdots$Au core, one Au atom occupying an endo position within the cup, the other Au occupying an exo position at the base of the cup (Figure 6.3(a)). The cations $87^{2+}$ form columns within the crystal, the base of one cup nestled within the opening of the next. This arrangement appears to be stabilised by weak intermolecular aurophilic interactions ($\text{Au}_{\text{endo}}\cdots\text{Au}_{\text{exo}} \ 3.6116(3) \ \text{Å}$) and two C-H$\cdots$S interactions (both 2.933(1) Å, between H5 atoms of the IMT units attached to the exo Au centre in one complex and the S atoms of the IMT units attached to the exo Au centre in the next complex along the column (Figure 6.3(b))).
Figure 6.3 (a) Crystal structure (50% probability level for the displacement ellipsoids) of the cation of 87·2PF₆. Selected bond lengths (Å) and angles (°): Au(1)-S(1) 2.2983(11), Au(1)-Au(2) 3.0505(3), Au(2)-S(2) 2.3012(11), S(1)-C(12) 1.724(4), S(2)-C(22) 1.723(4), S(1')-Au(1)-S(1) 173.37(5), S(2)-Au(2)-S(2') 169.98(5), S(1)-Au(1)···Au(2) 86.68(3), S(2)-Au(2)···Au(1) 95.01(3), C(12)-S(1)-Au(1) 102.70(14), C(22)-S(2)-Au(2) 105.60(14), where the prime refers to the atom generated by crystallographic 2-fold axis. (b) Two adjacent cations in the crystal structure of 87·2PF₆, showing inter-cation Au···Au and C-H···S contacts (3.6116(3) and 2.933(1) Å respectively).
In $\text{88}\cdot 2\text{Cl}^\dagger$ and $\text{89}\cdot 2\text{PF}_6$ (Figures 6.4 and 6.5), the cations $\text{88}^{2+}$ and $\text{89}^{2+}$ are again dinuclear, of form $\text{Au}_2\{\text{bis(IMT)}\}_2$. In both cations, the two $\text{S—Au—S}$ moieties are parallel, and the two thione moieties bound to each Au centre are oriented mutually \textit{anti}. There is no evidence of intramolecular aurophilic interactions, presumably due to the longer linker between the IMT units in the ligands. In $\text{88}^{2+}$ (Figure 6.4(a)), the intra-cation $\text{Au} \cdots \text{Au}$ distance is 4.3207(6) Å, but the two $\text{S—Au—S}$ moieties are offset, so that the each Au centre approaches one of the S atoms bound to the other Au centre ($\text{Au} \cdots \text{S}$ 3.700(3) Å). In $\text{89}^{2+}$ (Figure 6.5(a)), the Au centres are even more remote (intra-cation $\text{Au} \cdots \text{Au}$ 8.3839(5) Å). In both structures, the cations stack in columns. For $\text{88}\cdot 2\text{Cl}$, the columns align with $b$, each pair of cations $\text{88}^{2+}$ being linked by two $\text{Au} \cdots \text{S}$ contacts of 3.537(6) Å and two $\text{Au} \cdots \text{S}$ contacts of 3.557(3) Å (Figure 6.4(b)). For $\text{89}\cdot 2\text{PF}_6$, the columns lie along $c$, adjacent cations being linked by two $\text{Au} \cdots \text{S}$ contacts (3.481(2) Å) (Figure 6.5(b)).

\footnote{\textit{\dagger} For $\text{88}\cdot 2\text{Cl}$, the cation was modelled as being disordered over two sites with occupancies refined to 0.823 (3) and its complement. The two sites were broadly similar and only the major component is discussed here.}
Figure 6.4 (a) Crystal structure (50% probability level for the displacement ellipsoids) of the major component of the cation of $88 \cdot 2\text{Cl}$. Selected bond lengths (Å) and angles (°): Au(1)-S(1) 2.306(3), Au(1)-S(2') 2.310(5), Au(2)-S(3) 2.29(2), Au(2)-S(4'') 2.36(3), S(1)-Au(1)-S(2') 179.34(17), C(11)-S(1)-Au(1) 100.0(4), C(21)-S(2)-Au(1') 99.0(5), S(3)-Au(2)-S(4'') 176.3(8), C(31)-S(3)-Au(2) 98.9(10), C(41)-S(4)-Au(2'') 94(3), where the primes refer to the atoms related by crystallographic inversion centres. (b) Columnar arrangement of adjacent cations $88^{2+}$ (major component) in the crystal structure of $88 \cdot 2\text{Cl}$ (H atoms omitted for clarity), showing intercation Au···S contacts. Each pair of cations are linked by two Au···S contacts of 3.537(6) Å and two Au···S contacts of 3.557(3) Å.
Figure 6.5 (a) Crystal structure (50% probability level for the displacement ellipsoids) of the cation of $^{89}\text{AuPF}_6$. Selected bond lengths (Å) and angles (°): $\text{Au}(1)\cdots\text{S}(1)$ 2.288(2), $\text{Au}(1)\cdots\text{S}(2')$ 2.2938(18), $\text{S}(1)\cdots\text{C}(22)$ 1.724(8), $\text{S}(2)\cdots\text{C}(42)$ 1.729(7), $\text{S}(1)\cdots\text{Au}(1')\cdots\text{S}(2')$ 176.62(7), $\text{C}(22)\cdots\text{S}(1)\cdots\text{Au}(1)\cdots\text{S}(2')$ 100.8(3), $\text{C}(42)\cdots\text{S}(2)\cdots\text{Au}(1')$ 98.8(2), where the primes refer to the atoms related by the crystallographic inversion centre. (b) Columnar arrangement of adjacent cations $^{89}\text{Au}^{2+}$ in the crystal structure of $^{89}\text{AuPF}_6$ (H atoms omitted for clarity), showing inter-cation $\text{Au}\cdots\text{S}$ contacts. Each pair of cations are linked by two $\text{Au}\cdots\text{S}$ contacts of 3.481(2) Å.
The cation in 90·PF₆, the bis(IMT) ligand 80 chelates the Au centre to form a complex of form Au-bis(IMT). The cations are organised into trimers in which the Au centres form a triangular Au₃ core via aurophilic interactions (Au⋯Au 3.0356(5) - 3.0721(5) Å), and the ligands form a pinwheel-type arrangement around the Au₃ core (Figure 6.6). The cation in 93·Cl is also of form Au-bis(IMT), the ligand 81 again chelating the Au centre (Figure 6.7). While the ligands 80 and 81 both contain m-xylene-based linkers that place the IMT moieties sufficiently far apart to allow the ligand to be trans-spanning about the Au centre, the second m-xylene-based linker in 81 prevents formation of a trimer structure in the case of 93⁺. Indeed, the Au centre in 93⁺ is nestled in a pocket formed between the m-xylene-based linkers, and these linkers (in particular their methyl substituents) seem to inhibit approach of other Au centres, so that no aurophilic interactions occur.
Figure 6.6 Crystal structure (50% probability level for the displacement ellipsoids) of $^{90}\cdot{3}\text{PF}_6$. Selected bond lengths (Å) and angles (°): Au(1)-S(12) 2.310(2), Au(1)-S(14) 2.323(2), Au(2)-S(24) 2.321(2), Au(2)-S(22) 2.326(2), Au(3)-S(34) 2.310(2), Au(3)-S(32) 2.315(2), Au(4)-Cl(1) 2.264(6), Au(4)-Cl(2) 2.273(6), Au(1)···Au(2) 3.0528(5), Au(1)···Au(3) 3.0721(5), Au(2)···Au(3) 3.0356(5), S(12)-Au(1)-S(14) 168.10(7), S(24)-Au(2)-S(22) 168.08(8), S(34)-Au(3)-S(32) 169.07(7), Cl(1)-Au(4)-Cl(2) 179.75(19), C(122)-S(12)-Au(1) 97.4(3), C(142)-S(14)-Au(1) 93.7(3), C(222)-S(22)-Au(2) 95.0(3), C(242)-S(24)-Au(2) 94.9(3), C(322)-S(32)-Au(3) 94.6(3), C(342)-S(34)-Au(3) 96.8(3).
Chapter 6: Au$^+$ complexes of imidazole-2-thiones

Figure 6.7 Crystal structure (50% probability level for the displacement ellipsoids) of the cation of 93·Cl. Selected bond lengths (Å) and angles (°): Au(1)-S(2) 2.3087(10), Au(1)-S(1) 2.3140(10), S(1)-C(22) 1.733(4), S(2)-C(42) 1.731(5), S(2)-Au(1)-S(1) 176.05(4), C(22)-S(1)-Au(1) 96.10(13), C(42)-S(2)-Au(1) 98.30(14).

The ligand 33, like 80 and 81, contains m-xylylene-based linkers, but its Au complex 91 is distinct from those seen for the other ligands. Presumably 91 is the kinetic product of the reaction of (Me$_2$S)AuCl with anti-33, while the kinetic product of the reaction of syn-33 (see below) was not crystallised. Two distinct crystal types, denoted in the following discussion as 91' and 91'', were obtained. In 91', each IMT unit forms an adduct with AuCl, so the complex is of the form [bis(imidazole-2-thione)](AuCl)$_2$. The two Au centres are well-separated (Au···Au 7.0271(5) Å), the two S-Au-Cl moieties being mutually anti about the cyclophane skeleton (Figure 6.8(a)). The conformation may be stabilised by hydrogen bonding interactions between each
chlorido ligand and one of the imidazole H4/5 hydrogens on the opposing IMT moiety (C-H···Cl-Au 2.68 Å) (Figure 6.8(b)). Molecules of 91' are linked by intermolecular hydrogen bonding to form chains along b; each imidazole H4/5 hydrogen not involved in intramolecular H-bonding forms an intermolecular hydrogen bond to a chlorido ligand in a neighbouring molecule (C-H···Cl-Au 2.75 Å), so that adjacent molecules are linked by two such hydrogen bonds (Figure 6.8(c)). The structure for 91" is broadly similar. Within each complex, the Au···Au distance is 7.1582(4) Å, and again there is an intramolecular hydrogen bonding interaction (C-H···Cl-Au 2.728 Å) between each chlorido ligand and one of the imidazole H4/5 hydrogens on the opposing IMT moiety. In 91", however, the molecules are linked into chains by aurophilic interactions (Au···Au 2.9868(5) Å) (Figure 6.9).
Figure 6.8 (a) Crystal structure (50% probability level for the displacement ellipsoids) of the 91'. Selected bond lengths (Å) and angles (°): Au(1)-S(1) 2.2633(12), Au(1)-Cl(1) 2.2931(12), S(1)-C(1) 1.726(5), S(1)-Au(1)-Cl(1) 174.44(4), C(1)-S(1)-Au(1) 105.50(16), C(3)-H(3)···Cl(1) 2.75, C(4)-H(4)···Cl(1) 2.68, C(27)-H(27)A···S(1) 2.76, C(27)-H(27)B···Cl(1) 2.65. (b) Intramolecular H-bonding between each chlorido ligand and one of the imidazole H4/5 hydrogens in 91'. (c) Columnar arrangement of adjacent 91' molecules, showing intermolecular hydrogen bonding between an imidazole H4/5 hydrogen and a chlorido ligand in neighbouring molecules.
Figure 6.9 Crystal structure (50% probability level for the displacement ellipsoids) of the 91". Selected bond lengths (Å) and angles (°): Au(1)-S(1) 2.2770 (13), Au(1)-Cl(1) 2.3041 (12), Au(1)-Au(1)\textsuperscript{i} 2.9867 (4), S(1)-C(1) 1.733 (6), S(1)-Au(1)-Cl(1) 175.47 (5), S(1)-Au(1)-Au(1)\textsuperscript{i} 86.94 (4), Cl(1)-Au(1)-Au(1)\textsuperscript{i} 93.15 (4), C(1)-S(1)-Au(1) 102.43(17), H(3)···Cl(1)\textsuperscript{ii} 2.895, H(4)···Cl(1)\textsuperscript{iii} 2.728. The symmetry operations are: \textsuperscript{i} 1-x,y,1/2-z, \textsuperscript{ii} x,1-y,1/2+z, \textsuperscript{iii} 1-x,1-y,1-z
Table 6.1  Crystal data of 85·3Cl, 86·2Cl, 87·2PF₆, 88·2Cl, 89·2PF₆, 90·PF₆, 91', 91'' and 93·Cl.

<table>
<thead>
<tr>
<th>Complex*</th>
<th>85·3Cl</th>
<th>86·2Cl</th>
<th>87·2PF₆</th>
<th>88·2Cl</th>
<th>89·2PF₆</th>
<th>90·PF₆</th>
<th>91'</th>
<th>91''</th>
<th>93·Cl</th>
</tr>
</thead>
<tbody>
<tr>
<td>Empirical formula</td>
<td>C₁₂H₁₈Au₃Cl₅N₆O₃S₈</td>
<td>C₁₁H₂₀AuCl₅NS₂</td>
<td>C₈H₁₈Au₆F₁₆N₆P₃S₁</td>
<td>C₁₂H₂₄Au₆Cl₆F₁₆N₆P₃S₁</td>
<td>C₁₂H₂₄Au₆Cl₆F₁₆N₆P₃S₁</td>
<td>C₁₂H₂₄Au₆Cl₆F₁₆N₆P₃S₁</td>
<td>C₁₂H₂₄Au₆Cl₆F₁₆N₆P₃S₁</td>
<td>C₁₂H₂₄Au₆Cl₆F₁₆N₆P₃S₁</td>
<td>C₁₂H₂₄Au₆Cl₆F₁₆N₆P₃S₁</td>
</tr>
<tr>
<td>Formula weight</td>
<td>1726.29</td>
<td>516.86</td>
<td>1164.56</td>
<td>973.58</td>
<td>1344.80</td>
<td>2014.11</td>
<td>869.37</td>
<td>869.37</td>
<td>771.17</td>
</tr>
<tr>
<td>Wavelength / Å</td>
<td>0.71073</td>
<td>0.71073</td>
<td>0.71073</td>
<td>1.54184</td>
<td>1.54178</td>
<td>1.54184</td>
<td>0.71073</td>
<td>0.71073</td>
<td>0.71073</td>
</tr>
<tr>
<td>Crystal system</td>
<td>Monoclinic</td>
<td>Orthorhombic</td>
<td>Monoclinic</td>
<td>Monoclinic</td>
<td>Monoclinic</td>
<td>Triclinic</td>
<td>Triclinic</td>
<td>Monoclinic</td>
<td>Triclinic</td>
</tr>
<tr>
<td>Space group</td>
<td>P2₁/c</td>
<td>Fddd</td>
<td>C2/c</td>
<td>P2/n</td>
<td>P2₁/c</td>
<td>P2₁</td>
<td>C2/c</td>
<td>pT</td>
<td></td>
</tr>
<tr>
<td>b / Å</td>
<td>19.0687(2)</td>
<td>23.612(5)</td>
<td>6.6622(1)</td>
<td>4.4841(2)</td>
<td>15.9149(5)</td>
<td>14.8353(8)</td>
<td>8.7617(4)</td>
<td>9.1185(2)</td>
<td>10.3386(4)</td>
</tr>
<tr>
<td>c / Å</td>
<td>13.4244(2)</td>
<td>39.001(5)</td>
<td>22.1246(6)</td>
<td>22.3012(7)</td>
<td>10.4964(2)</td>
<td>17.4580(7)</td>
<td>9.1405(4)</td>
<td>15.6233(4)</td>
<td>17.0080(6)</td>
</tr>
<tr>
<td>α°</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>65.886(4)</td>
<td>110.92(4)</td>
<td>-</td>
<td>100.45(3)</td>
</tr>
<tr>
<td>β°</td>
<td>92.684(4)</td>
<td>-</td>
<td>112.190(4)</td>
<td>94.193(3)</td>
<td>90.871(2)</td>
<td>84.529(3)</td>
<td>92.524(4)</td>
<td>108.845(3)</td>
<td>98.669(3)</td>
</tr>
<tr>
<td>γ°</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>60.663(5)</td>
<td>108.88(4)</td>
<td>-</td>
<td>100.18(3)</td>
</tr>
<tr>
<td>V / Å³</td>
<td>2698.43(6)</td>
<td>14898(6)</td>
<td>3196.73(17)</td>
<td>1422.68(9)</td>
<td>2178.39(9)</td>
<td>3000.8(3)</td>
<td>601.44(5)</td>
<td>2335.02(11)</td>
<td>1483.25(9)</td>
</tr>
<tr>
<td>Z</td>
<td>2</td>
<td>32</td>
<td>4</td>
<td>2</td>
<td>2</td>
<td>2</td>
<td>1</td>
<td>4</td>
<td>2</td>
</tr>
<tr>
<td>ρ calc/Mg m⁻³</td>
<td>2.058</td>
<td>1.843</td>
<td>2.420</td>
<td>2.273</td>
<td>2.050</td>
<td>2.223</td>
<td>2.400</td>
<td>2.473</td>
<td>1.727</td>
</tr>
<tr>
<td>μ / mm⁻¹</td>
<td>8.756</td>
<td>8.263</td>
<td>9.628</td>
<td>23.809</td>
<td>15.764</td>
<td>20.040</td>
<td>12.597</td>
<td>12.997</td>
<td>5.224</td>
</tr>
<tr>
<td>Crystal size / mm³</td>
<td>0.38 × 0.15 × 0.08</td>
<td>0.55 x 0.43 x 0.32</td>
<td>0.31 x 0.04 x 0.02</td>
<td>0.262 x 0.043 x 0.034</td>
<td>0.18 x 0.09 x 0.03</td>
<td>0.056 x 0.034 x 0.021</td>
<td>0.32 x 0.13 x 0.05</td>
<td>0.115 x 0.053 x 0.023</td>
<td>0.43 x 0.08 x 0.05</td>
</tr>
<tr>
<td>0 range for data collection°</td>
<td>2.21 to 34.90</td>
<td>3.70 to 32.00</td>
<td>3.20 to 32.77</td>
<td>3.56 to 67.20</td>
<td>3.39 to 67.23</td>
<td>2.797 to 67.34</td>
<td>2.43 to 32.63</td>
<td>3.06 to 32.14</td>
<td>2.86 to 32.16</td>
</tr>
<tr>
<td>Reflections collected</td>
<td>71998</td>
<td>36556</td>
<td>33505</td>
<td>5663</td>
<td>11325</td>
<td>27118</td>
<td>12627</td>
<td>23296</td>
<td>30172</td>
</tr>
<tr>
<td>Independent reflections</td>
<td>11338</td>
<td>6288</td>
<td>5608</td>
<td>2518</td>
<td>3869</td>
<td>10699</td>
<td>4029</td>
<td>3950</td>
<td>9694</td>
</tr>
<tr>
<td>Complex&lt;sup&gt;a&lt;/sup&gt;</td>
<td>85·3Cl</td>
<td>86·2Cl</td>
<td>87·2PF₆</td>
<td>88·2Cl</td>
<td>89·2PF₆</td>
<td>90·PF₆</td>
<td>91'</td>
<td>91''</td>
<td>93·Cl</td>
</tr>
<tr>
<td>----------------------</td>
<td>--------</td>
<td>--------</td>
<td>--------</td>
<td>--------</td>
<td>--------</td>
<td>--------</td>
<td>------</td>
<td>-------</td>
<td>-------</td>
</tr>
<tr>
<td>R(int)</td>
<td>0.0596</td>
<td>0.0555</td>
<td>0.0668</td>
<td>0.0670</td>
<td>0.0478</td>
<td>0.0489</td>
<td>0.0482</td>
<td>0.0707</td>
<td>0.0575</td>
</tr>
<tr>
<td>Max. /Min. Transmission</td>
<td>1.0'/0.117</td>
<td>0.237'/0.087</td>
<td>1.0'/0.706</td>
<td>0.547'/0.136</td>
<td>1.0'/0.303</td>
<td>0.747'/0.495</td>
<td>0.552'/0.158</td>
<td>1.0'/0.530</td>
<td>0.799'/0.363</td>
</tr>
<tr>
<td>Restraints / Parameters</td>
<td>3'/295</td>
<td>75'/187</td>
<td>0'/211</td>
<td>81'/229</td>
<td>138'/335</td>
<td>108'/848</td>
<td>0'/146</td>
<td>0'/145</td>
<td>4'/366</td>
</tr>
<tr>
<td>Goodness-of-fit on $R^2$</td>
<td>1.000</td>
<td>1.089</td>
<td>1.002</td>
<td>1.041</td>
<td>1.003</td>
<td>1.037</td>
<td>1.000</td>
<td>1.002</td>
<td>1.004</td>
</tr>
<tr>
<td>$R_1$ [I &gt; 2σ(I)]</td>
<td>0.0328</td>
<td>0.1123</td>
<td>0.0370</td>
<td>0.0630</td>
<td>0.0413</td>
<td>0.0420</td>
<td>0.0345</td>
<td>0.0388</td>
<td>0.0409</td>
</tr>
<tr>
<td>wR2[I &gt; 2σ(I)]</td>
<td>0.0659</td>
<td>0.2825</td>
<td>0.0745</td>
<td>0.1563</td>
<td>0.1006</td>
<td>0.0916</td>
<td>0.0725</td>
<td>0.0851</td>
<td>0.0957</td>
</tr>
<tr>
<td>$R_1$ (all data)</td>
<td>0.0698</td>
<td>0.1538</td>
<td>0.0370</td>
<td>0.0746</td>
<td>0.0549</td>
<td>0.0603</td>
<td>0.0421</td>
<td>0.0559</td>
<td>0.0505</td>
</tr>
<tr>
<td>wR2 (all data)</td>
<td>0.0799</td>
<td>0.3088</td>
<td>0.0806</td>
<td>0.1695</td>
<td>0.1125</td>
<td>0.1001</td>
<td>0.0784</td>
<td>0.0942</td>
<td>0.1014</td>
</tr>
<tr>
<td>$\Delta$ρ(max/min)/eÅ&lt;sup&gt;3&lt;/sup&gt;</td>
<td>4.80'/-1.81</td>
<td>5.52'/-5.52</td>
<td>2.09'/-1.31</td>
<td>2.79'/-2.45</td>
<td>2.01'/-0.67</td>
<td>1.90'/-1.04</td>
<td>3.63'/-2.62</td>
<td>2.68'/-1.82</td>
<td>2.97'/-1.92</td>
</tr>
<tr>
<td>CCDC Number</td>
<td>1573930</td>
<td>1573929</td>
<td>1573931</td>
<td>1573932</td>
<td>1573933</td>
<td>1573934</td>
<td>1573935</td>
<td>1573936</td>
<td>1573937</td>
</tr>
</tbody>
</table>

<sup>a</sup> Empirical formula of crystals: 85·Cl(H₂O)₀.67(CH₂Cl₂)₀.67, 86·Cl, 87·2PF₆, 88·2Cl, 89·2PF₆, 90·(AuCl₂)₀.203Cl₀.260(PF₆)₀.537(H₂O)₀.130, 91', 91'', 93·Cl(CH₃OH)(H₂O).
### Chapter 6: Au(I) complexes of imidazole-2-thiones

#### Table 6.2  
Bond Lengths (Å) and angles (°) in Au(I)-IMT complexes.

<table>
<thead>
<tr>
<th>Complex</th>
<th>Au-S</th>
<th>S-C</th>
<th>Au···Au</th>
<th>S-Au-S</th>
<th>C-S-Au</th>
<th>θ°</th>
</tr>
</thead>
<tbody>
<tr>
<td>(18^{+22})</td>
<td>2.287(3)</td>
<td>1.705(9)</td>
<td>5.665(1)</td>
<td>180.0</td>
<td>110.3(3)</td>
<td>13.86</td>
</tr>
<tr>
<td>(19^{23})</td>
<td>2.269(2)</td>
<td>1.717(8)</td>
<td>-</td>
<td>-</td>
<td>103.8(2)</td>
<td>-</td>
</tr>
<tr>
<td>(85\cdot3\text{Cl})</td>
<td>2.3178(9)</td>
<td>1.729(3)</td>
<td>3.0466(1)</td>
<td>180.0</td>
<td>103.10(11)</td>
<td>71.75</td>
</tr>
<tr>
<td></td>
<td>2.2875(9)</td>
<td>1.719(3)</td>
<td>172.46(3)</td>
<td>106.15(12)</td>
<td>75.52</td>
<td></td>
</tr>
<tr>
<td></td>
<td>2.2958(9)</td>
<td>1.733(4)</td>
<td>106.66(12)</td>
<td>85.64</td>
<td></td>
<td></td>
</tr>
<tr>
<td>(86\cdot2\text{Cl})</td>
<td>2.225(18)</td>
<td>1.57(3)</td>
<td>3.0647(12)</td>
<td>172.5(5)</td>
<td>104.5(13)</td>
<td>61.16</td>
</tr>
<tr>
<td></td>
<td>2.240(7)</td>
<td>1.68(2)</td>
<td>175.8(5)</td>
<td>108.2(10)</td>
<td>71.63</td>
<td></td>
</tr>
<tr>
<td></td>
<td>2.323(15)</td>
<td></td>
<td></td>
<td>103.7(11)</td>
<td>71.81</td>
<td></td>
</tr>
<tr>
<td></td>
<td>2.432(11)</td>
<td></td>
<td></td>
<td>100.6(8)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>(87\cdot2\text{PF}_6)</td>
<td>2.2983(11)</td>
<td>1.723(4)</td>
<td>3.0505(3)</td>
<td>169.98(5)</td>
<td>102.70(14)</td>
<td>87.23</td>
</tr>
<tr>
<td></td>
<td>2.3012(11)</td>
<td>1.724(4)</td>
<td>173.37(5)</td>
<td>105.60(14)</td>
<td>89.83</td>
<td></td>
</tr>
<tr>
<td>(88\cdot2\text{Cl})</td>
<td>2.29(2)</td>
<td>1.73(1)</td>
<td>4.3207(6)</td>
<td>176.3(8)</td>
<td>99.0(5)</td>
<td>76.96</td>
</tr>
<tr>
<td></td>
<td>2.306(3)</td>
<td>1.75(1)</td>
<td>179.34(17)</td>
<td>100.0(4)</td>
<td>84.38</td>
<td></td>
</tr>
<tr>
<td></td>
<td>2.310(5)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>2.36(3)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(89\cdot2\text{PF}_6)</td>
<td>2.288(2)</td>
<td>1.724(8)</td>
<td>8.3839(5)</td>
<td>176.62(7)</td>
<td>98.8(2)</td>
<td>79.87</td>
</tr>
<tr>
<td></td>
<td>2.2938(18)</td>
<td>1.729(7)</td>
<td>100.8(3)</td>
<td>80.71</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Complex</td>
<td>Au-S</td>
<td>S-C</td>
<td>Au···Au</td>
<td>S-Au-S</td>
<td>C-S-Au</td>
<td>$\theta^\circ$</td>
</tr>
<tr>
<td>----------</td>
<td>-------</td>
<td>------</td>
<td>---------</td>
<td>--------</td>
<td>--------</td>
<td>----------------</td>
</tr>
<tr>
<td>90·PF$_6$</td>
<td>2.310(2)</td>
<td>1.734(8)</td>
<td>3.0356(5)</td>
<td>168.10(7)</td>
<td>94.6(3)</td>
<td>85.51</td>
</tr>
<tr>
<td></td>
<td>2.323(2)</td>
<td>1.756(9)</td>
<td>3.0528(5)</td>
<td>168.08(8)</td>
<td>96.8(3)</td>
<td>83.05</td>
</tr>
<tr>
<td></td>
<td>2.321(2)</td>
<td>1.743(9)</td>
<td>3.0721(5)</td>
<td>169.07(7)</td>
<td>97.4(3)</td>
<td>84.59</td>
</tr>
<tr>
<td></td>
<td>2.326(2)</td>
<td>1.751(9)</td>
<td></td>
<td>93.7(4)</td>
<td>86.63</td>
<td></td>
</tr>
<tr>
<td></td>
<td>2.315(2)</td>
<td>1.742(9)</td>
<td></td>
<td>95.0(3)</td>
<td>85.65</td>
<td></td>
</tr>
<tr>
<td></td>
<td>2.310(2)</td>
<td>1.739(8)</td>
<td></td>
<td>94.9(4)</td>
<td>80.23</td>
<td></td>
</tr>
<tr>
<td>91'</td>
<td>2.2633(12)</td>
<td>1.726(5)</td>
<td>-</td>
<td>2.2931(12)</td>
<td>105.50(16)</td>
<td>-</td>
</tr>
<tr>
<td>91''</td>
<td>2.2770(13)</td>
<td>1.733(6)</td>
<td>2.9867(4)</td>
<td>2.3041(12)</td>
<td>102.43(17)</td>
<td>-</td>
</tr>
<tr>
<td>93·Cl</td>
<td>2.3087(10)</td>
<td>1.733(4)</td>
<td>-</td>
<td>176.05(4)</td>
<td>96.10(13)</td>
<td>87.82</td>
</tr>
<tr>
<td></td>
<td>2.3140(10)</td>
<td>1.731(5)</td>
<td></td>
<td>98.30(14)</td>
<td>89.04</td>
<td></td>
</tr>
</tbody>
</table>

$^a$ $\theta = \text{AuS}_2$ / IMT inter-planar angle
6.4 Mass spectrometry studies

The solution behaviour of the new ligands and complexes has been investigated using mass spectrometry, in part to aid in interpretation of NMR spectra (see below). Mass spectra of ligands were unexceptional – all showed the expected molecular ions in APCI-MS recorded from acetonitrile solutions. For most of the new complexes, molecular ions seen in ESI-MS from acetonitrile solutions were consistent with the presence of complex cations expected on the basis of the X-ray studies. For example, for 85\textsuperscript{·}Cl, 86\textsuperscript{·}Cl, 92\textsuperscript{·}Cl, and 93\textsuperscript{·}Cl, molecular ion corresponding to 85\textsuperscript{+}, 86\textsuperscript{+}, 92\textsuperscript{+}, and 93\textsuperscript{+} were seen, while for 87\textsuperscript{·}2Cl and 88\textsuperscript{·}2Cl, pseudomolecular ions corresponding to [87\textsuperscript{·}Cl]\textsuperscript{+} and [88\textsuperscript{·}Cl]\textsuperscript{+} were seen. Results for 89\textsuperscript{·}2PF\textsubscript{6} suggested that in solution the dominant Au complex is not the cationic dimer 89\textsuperscript{2+} — in the ESI and APCI mass spectra obtained from a acetonitrile or methanol solutions of 89\textsuperscript{·}2PF\textsubscript{6}, the dominant ion occurred near m/z = 527.063, with associated isotopomers appearing at m/z near 528, 529, and 530. These results suggest that the dominant complex in solution is a mononuclear complex 89\textsubscript{m}\textsuperscript{+} (m/z calc'd = 527.0639). A weak signal was seen near m/z = 1199.08, which corresponds to [89\textsuperscript{·}PF\textsubscript{6}]\textsuperscript{+} (m/z calc'd = 1199.0919), suggesting that in solution the dinuclear cation 89\textsuperscript{2+} and the mononuclear cation 89\textsubscript{m}\textsuperscript{+} are in fact in equilibrium, the mononuclear form being favoured. ESI and APCI studies of 90\textsuperscript{·}PF\textsubscript{6} in acetonitrile and methanol solutions indicated that in this case mononuclear (90\textsuperscript{+}) and dinuclear (90\textsubscript{d}\textsuperscript{2+}) cations also existed in equilibrium in solution, the mononuclear form being favoured in this case too, but in this case it was the mononuclear type that was seen in the X-ray study (above).
6.5 NMR studies

NMR spectra for the new Au-NHC complexes are summarized in Tables 6.3 and 6.4 and Figures 6.11-13. The new Au complexes of imidazole-2-thiones exhibited NMR spectra that are generally consistent with the structures of cations of form [AuL₂]⁺ or [Au₂L₂]²⁺ as seen in the solid state (but see discussion for 89·2PF₆ and 90·PF₆ below).

In the ¹H NMR spectra, the chemical shifts of the H4 and H5 of the imidazole-2-thione groups in the complexes were in the range 7.10-7.86 ppm, ca. 0.45 ppm downfield of the corresponding protons in the free ligands, presumably due to a decrease in electron density in the heterocyclic ring upon coordination of the thione moieties to Au. In the ¹³C NMR spectra, the signal due to the C=S group appeared near 152 ppm, about 10 ppm upfield of the signal for the C=S group in the free ligands.

Curiously, for the most of the Au-thione complexes (but not the free IMT ligands), the ¹³C NMR signal for C=S carbon is broad, apparently a consequence of rapid Au-thione exchange reactions in solution. Such exchange reactions are well-known for Au¹ complexes involving sulfur-donor ligands.²⁵-²⁷ To test for the
existence of rapid exchange processes, DMSO-d$_6$ solutions of 85·Cl and 86·Cl were mixed and the $^1$H NMR spectrum of the mixture was recorded immediately. The $^1$H NMR spectrum of the mixture showed no signals that could be attributed to either 85$^+$ or 86$^+$ or the mixed ligand complex 96$^+$ (Scheme 6.1). Only one set of signals due to 1,3-dimethylimidazole-2-thione ligands was seen, a result which may be attributed to the time-average of signals for 1,3-dimethylimidazole-2-thione in 85$^+$ and 96$^+$, and likewise only one set of signals was seen for 1-ethyl-3-methylimidazole-2-thione ligands, which can be attributed to the time-average of signals for 1-ethyl-3-methylimidazole-2-thione in 86$^+$ and 96$^+$. Similar results were seen in $^{13}$C NMR spectra, but with signals corresponding to the imidazole C4 and C5 carbons becoming significantly broadened, and signals corresponding to the imidazole C2 apparently being too broad to detect. When DMSO-d$_6$ solutions of 82 and 85·Cl were mixed and the $^1$H NMR spectrum was recorded immediately, all signals for IMT units broadened, consistent with exchange of free and Au-bound ligands occurring at a rate comparable to the NMR timescale (Figure 6.10).

Scheme 6.1  Exchange reaction between 85·Cl and 86·Cl complexes
Figure 6.10 $^1$H NMR spectra (DMSO-$d_6$, 500.10 MHz) of:

(a) a freshly prepared solution of 85·Cl;
(b) a freshly prepared solution of 82;
(c) A mixture solution of 85·Cl and 82.
For 87·2Cl in DMSO-d₆ solution at room temperature, the ¹H NMR signals were broad at room temperature but sharpened when the temperature was increased (Figure 6.11). It is of note that the methylene protons appeared as a singlet, indicating that the conformation seen in the solid state (in which each methylene group has an \textit{exo} and \textit{endo} proton environment) is fluxional in solution. Similar ¹H NMR spectra were seen for 88·2Cl were analogous to those seen for 87·2Cl but in this case the signals were sharper, consistent with the larger Au₂L₂ macrocycle in 88²⁺ being more conformationally labile than that in 87²⁺.
In the $^1$H NMR spectra of solutions of 91, 92·Cl and 93·Cl, AX patterns are seen for the exo and endo protons in of the benzylic CH$_2$ groups. This result indicates that the cyclophane bis(thione) ligands in the complexes are conformationally somewhat rigid in solution. In the $^1$H NMR spectrum of 93·Cl in DMSO-$d_6$ solution (Figure 6.12(a)) the imidazolyl H4/5 protons appear as a singlet at 7.86 ppm, far downfield of signal for the H4/H5 protons in the unbound ligand 81 (5.63 ppm; Figure 6.12(b)). The large
difference in these chemical shifts is likely due, at least in part, to cyclophane ligand in 93\(^+\) existing in the 1,3-alternate type conformation (seen in the solid state). This conformation places the imidazolium H4/H5 protons far from the shielding effects of the benzene rings, whereas the free cyclophane 81 exists in a cone conformation that places the H4/H5 protons in a region of shielding by the ring currents of the benzene rings. Interestingly, the \(^{13}\)C NMR signal for the C=S group in 93·Cl is sharp, presumably because the mesitylene rings in the cyclophane ligand shield the Au centre, thereby inhibiting any ligand exchange reactions.

![Diagram of 93·Cl and 81](image)

**Figure 6.12** \(^1\)H NMR spectra (600 MHz, DMSO-\(d_6\)) for solutions of (a) the Au\(^I\) complex 93·Cl (b) the ligand 81.
For the inseparable mixture of \(91\) and \(92\)·Cl, the \(^1\)H NMR spectrum in DMSO-\(d_6\) solution at room temperature (Figure 6.13(a)) shows two sets of signals, integration suggesting the presence of complexes in a ratio of \(ca.\ 2:1\). The minor set of signals is sharp and is attributed to the cation \(92^+\). Consistent with that assignment, the minor set includes an AB multiplet corresponding to the protons in the four equivalent methylene groups (one \(exo\) and one \(endo\) proton environment in each) and a sharp singlet for the four equivalent imidazolyl H4/H5 protons. The downfield chemical shift of the imidazolyl H4/H5 protons (~7.75 ppm) is consistent with a conformation in which these protons are oriented away from the shielding effects of the magnetic ring currents of the \(C_6H_4\) groups, analogous to the situation for \(93\)·Cl. The finding that the \(exo\) and one \(endo\) benzylic protons in \(92^+\) have distinct, sharp signals indicates that, as was seen for \(93^+\), the cyclophane ligand in \(92^+\) shields the Au centre, thereby inhibiting any ligand exchange reactions. Consistent with this notion, the C=S signal in the \(^{13}\)C NMR spectrum of \(92^+\) is also sharp. The major set of signals is broader, and is attributed to the dinuclear complex \(91\), existing in the \(anti\) conformation seen in the solid state. The broadness is likely due to a ring flip process (Scheme 6.2) and, as expected, the signals sharpen as the temperature is increased (Figure 6.13(b,c)). Poor solubility prevented NMR studies of this process below room temperature, while decomposition of the sample (accompanied by formation of colloidal Au) prevented detailed studies at high temperature. It should be noted, however, that the chemical shift of the H4/H5 protons in the major component (~7.15 ppm) is upfield of that seen for the minor component, consistent with each of these protons being shielded by the ring current of one of the \(C_6H_4\) groups (i.e., \(anti\) conformation, Scheme 6.2).
Scheme 6.2  Flipping of the arene rings in the anti conformation for 91

Figure 6.13  $^1$H NMR spectra of 91 and 92$^+$ (600 MHz, DMSO-$d_6$) at various temperatures from 25 to 80 °C.
The $^1$H NMR spectra for DMSO-$d_6$ or CD$_3$CN solutions of 89·2PF$_6$ and 90·PF$_6$ or their chloride analogs were similar, and, interestingly, showed only sharp singlets for the benzylic protons (e.g., Figure 6.14). In view of the mass spectrometry studies of solutions of 89·2PF$_6$ and 90·PF$_6$, and experiments demonstrating rapid ligand exchange between 85$^+$ and 86$^+$ (see above), these $^1$H NMR signals are likely to be averages of rapidly exchanging mononuclear and dinuclear complexes (89m$^+$ and 89$^{2+}$ or 90$^+$ and 90d$^{2+}$), the mononuclear forms being dominant. Not surprisingly, the C=S $^{13}$C NMR signals were broad in both cases.

Figure 6.14 $^1$H NMR spectra (500 MHz, DMSO-$d_6$) for: (a) the solution prepared by dissolving 90·PF$_6$ in DMSO-$d_6$; (b) the ligand 80.
<table>
<thead>
<tr>
<th>Complex</th>
<th>CH₃</th>
<th>CH₂</th>
<th>H4/H5</th>
<th>Aromatics</th>
</tr>
</thead>
<tbody>
<tr>
<td>85·Cl</td>
<td>3.66 (12H, s)</td>
<td>-</td>
<td>7.39 (4H, s)</td>
<td>-</td>
</tr>
<tr>
<td>86·Cl</td>
<td>1.29 (6H, t, $^3$$J_{H,H}$ 7.5), 4.11 (4H, q, $^3$$J_{H,H}$ 7.5)</td>
<td>3.64 (6H, s)</td>
<td>7.38-7.42 (4H, d, $^3$$J_{H,H}$ 17)</td>
<td>-</td>
</tr>
<tr>
<td>87·2Cl</td>
<td>3.50 (12H, s)</td>
<td>6.17 (4H, s)</td>
<td>7.39 (4H, d, $^3$$J_{H,H}$ 2.5), 7.10 (4H, br s)</td>
<td>-</td>
</tr>
<tr>
<td>88·2Cl</td>
<td>3.66 (12H, s)</td>
<td>4.58 (8H, s)</td>
<td>7.30 (4H, br s), 7.17 (4H, br s)</td>
<td>-</td>
</tr>
<tr>
<td>89·2PF₆</td>
<td>3.69 (12H, s)</td>
<td>5.52 (8H, s)</td>
<td>7.50 (4H, d, $^3$$J_{H,H}$ 2)</td>
<td>7.33-7.31, 6.97-6.95 (8H, AX pattern)</td>
</tr>
</tbody>
</table>

*H NMR data$^a$ for complexes 85·Cl, 86·Cl, 87·2Cl, 88·2Cl, 89·2PF₆, 90·PF₆, 91·Cl, 92·Cl and 93·Cl*
<table>
<thead>
<tr>
<th>Complex</th>
<th>CH&lt;sub&gt;3&lt;/sub&gt;</th>
<th>CH&lt;sub&gt;2&lt;/sub&gt;</th>
<th>H4/H5</th>
<th>Aromatics</th>
</tr>
</thead>
<tbody>
<tr>
<td>90·PF&lt;sub&gt;6&lt;/sub&gt;</td>
<td>3.78 (6H, s)</td>
<td>5.42 (4H, s)</td>
<td>7.81 (2H, d, &lt;sup&gt;3&lt;/sup&gt;J&lt;sub&gt;H,H&lt;/sub&gt; 2)</td>
<td>7.45 (1H, br s), 7.46 (2H, br s), 7.40 (1H, s)</td>
</tr>
<tr>
<td>91&lt;sup&gt;d&lt;/sup&gt;</td>
<td>-</td>
<td>5.71 (4H, d, &lt;sup&gt;2&lt;/sup&gt;J&lt;sub&gt;H,H&lt;/sub&gt; 16.2)</td>
<td>7.15 (4H, s)</td>
<td>7.43 (2H, t, &lt;sup&gt;3&lt;/sup&gt;J&lt;sub&gt;H,H&lt;/sub&gt; 7.5), 7.33 (4H, d, &lt;sup&gt;3&lt;/sup&gt;J&lt;sub&gt;H,H&lt;/sub&gt; 7.5), 6.35 (2H, s)</td>
</tr>
<tr>
<td>92·Cl</td>
<td>-</td>
<td>5.60-5.49 (8H, AB, &lt;sup&gt;2&lt;/sup&gt;J&lt;sub&gt;H,H&lt;/sub&gt; 16.5)</td>
<td>7.75 (4H, s)</td>
<td>7.53 (2H, t, &lt;sup&gt;3&lt;/sup&gt;J&lt;sub&gt;H,H&lt;/sub&gt; 7.5), 7.44 (4H, d, &lt;sup&gt;3&lt;/sup&gt;J&lt;sub&gt;H,H&lt;/sub&gt; 7.5), 6.17 (2H, s)</td>
</tr>
<tr>
<td>93·Cl</td>
<td>2.43 (12H, s)</td>
<td>5.37 (4H, d, &lt;sup&gt;2&lt;/sup&gt;J&lt;sub&gt;H,H&lt;/sub&gt; 16)</td>
<td>7.86 (4H, s)</td>
<td>6.83 (2H, s)</td>
</tr>
<tr>
<td>94&lt;sup&gt;+&lt;/sup&gt;</td>
<td>-</td>
<td>5.87 (8H, br s)</td>
<td>5.80 (4H, s)</td>
<td>7.67-7.53 (16H, AA'XX' pattern)</td>
</tr>
</tbody>
</table>

<sup>a</sup> Recorded at 500.10 MHz and ambient temperature from solutions in DMSO-<em>d</em><sub>6</sub>.  
<sup>b</sup> Recorded at 600.13 MHz and ambient temperature from solutions in DMSO-<em>d</em><sub>6</sub>.  
<sup>c</sup> Recorded at 500.10 MHz and 65 °C from solutions in DMSO-<em>d</em><sub>6</sub>.  
<sup>d</sup> Recorded at 600.13 MHz and 80 °C from solutions in DMSO-<em>d</em><sub>6</sub>.  

Recorded at 500.10 MHz and ambient temperature from solutions in DMSO-<em>d</em><sub>6</sub>.
### Table 6.4 \(^{13}\)C NMR Data\(^a\) for complexes 85·Cl, 86·Cl, 87·2Cl, 88·2Cl, 89·2PF\(_6\), 90·PF\(_6\), 91, 92·Cl and 93·Cl

<table>
<thead>
<tr>
<th>Complex</th>
<th>C=S</th>
<th>Imidazolyl C4/C5</th>
<th>Benzylics</th>
<th>Aromatics</th>
<th>CH(_2)</th>
<th>CH(_3)</th>
</tr>
</thead>
<tbody>
<tr>
<td>85·Cl(^b)</td>
<td>152.27</td>
<td>120.67</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>35.39</td>
</tr>
<tr>
<td>86·Cl</td>
<td>152.72</td>
<td>121.28, 119.34</td>
<td>-</td>
<td>-</td>
<td>43.38</td>
<td>35.60</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>14.77</td>
</tr>
<tr>
<td>87·2Cl(^b)</td>
<td>148.47</td>
<td>123.82, 122.34</td>
<td>-</td>
<td>-</td>
<td>59.38</td>
<td>36.36</td>
</tr>
<tr>
<td>88·2Cl(^b)</td>
<td>153.83</td>
<td>121.18, 119.59</td>
<td>-</td>
<td>-</td>
<td>46.72</td>
<td>35.39</td>
</tr>
<tr>
<td>89·2PF(_6)</td>
<td>153.95</td>
<td>121.28, 119.82</td>
<td>48.31</td>
<td>133.35 (C)</td>
<td>-</td>
<td>35.46</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>128.27 (CH)</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>127.84 (CH)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>90·PF(_6)(^b)</td>
<td>152.06</td>
<td>121.59, 120.18</td>
<td>50.61</td>
<td>135.87 (C)</td>
<td>-</td>
<td>35.52</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>129.21 (CH)</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>127.19 (CH)</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>126.92 (CH)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>91(^b)</td>
<td>c</td>
<td>121.51</td>
<td>50.46</td>
<td>136.64 (C)</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>128.97 (CH)</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>126.73 (CH)</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>121.28 (CH)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>92·Cl(^b)</td>
<td>148.97</td>
<td>123.06</td>
<td>51.23</td>
<td>134.71 (C)</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>129.36 (CH)</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>126.54 (CH)</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>120.79 (CH)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Complex</td>
<td>C=S</td>
<td>Imidazolyl C4/C5</td>
<td>Benzylics</td>
<td>Aromatics</td>
<td>CH₂</td>
<td>CH₃</td>
</tr>
<tr>
<td>---------</td>
<td>---------</td>
<td>------------------</td>
<td>-----------</td>
<td>-----------</td>
<td>---------</td>
<td>---------</td>
</tr>
<tr>
<td>93·Cl</td>
<td>146.78</td>
<td>123.85</td>
<td>48.74</td>
<td>138.60 (C)</td>
<td>-</td>
<td>20.53</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>135.81 (C)</td>
<td>129.95</td>
<td>18.20</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>129.46 (CH)</td>
<td></td>
</tr>
</tbody>
</table>

* Recorded at 125.75 MHz and ambient temperature from solutions in DMSO-d₆.

* Recorded at 150.90 MHz and ambient temperature from solutions in DMSO-d₆.

* Not seen.

### 6.6 Electronic absorption and emission spectroscopy

The new Au⁺ complexes 85·Cl - 90·PF₆ and 93·Cl have been characterised by UV–Vis spectroscopy in acetonitrile solutions (Figure 6.15 and Table 6.5). Each of the compounds showed intense absorption at high energy in the range of λ = 220-320 nm, which can be assigned to π-π* ligand-centred transitions.²⁸ For gold complexes, Au⁺ species do not display low energy metal-centred transitions because their d¹⁰ electron configuration.²⁹ Huynh et al. recently reported Au⁺⁺ halido complexes bearing imidazolin-2-ylidene ligands showing a broad band at 300-400 nm, tentatively assigned to a ligand-to-metal-charge-transfer (LMCT) of the halido ligands to the metal centre.²⁸ Such bands were also seen for the halido Au⁺⁺-NHC and halido Au⁺/Au⁺⁺-NHC complexes discussed in Chapter 2 and for the [Au(NHC)₄Cl₂]⁺ complexes discussed in Chapter 3, but not for the [Au(NHC)₄]³⁺ complexes discussed in Chapter 3.
Figure 6.15  UV-Vis absorption spectra of the Au\textsuperscript{I}-IMT complexes (0.010 mM in MeCN).

Table 6.5  UV–Vis Spectroscopic Data of Au\textsuperscript{I}-IMT Complexes \textsuperscript{a}

<table>
<thead>
<tr>
<th>Complexes</th>
<th>$\lambda_{\text{max}}$ / nm ((\varepsilon) / M\textsuperscript{-1} cm\textsuperscript{-1}) \textsuperscript{a}</th>
</tr>
</thead>
<tbody>
<tr>
<td>85·Cl</td>
<td>251 (59000)</td>
</tr>
<tr>
<td>86·Cl</td>
<td>252 (68000)</td>
</tr>
<tr>
<td>87·2Cl</td>
<td>237 (22000), 268 (41000)</td>
</tr>
<tr>
<td>88·2Cl</td>
<td>244 (39000), 264 (34000)</td>
</tr>
<tr>
<td>89·2PF\textsubscript{6}</td>
<td>242 (20500), 275 (28500)</td>
</tr>
<tr>
<td>90·PF\textsubscript{6}</td>
<td>254 (55000)</td>
</tr>
<tr>
<td>93·Cl</td>
<td>267 (12000)</td>
</tr>
</tbody>
</table>

\textsuperscript{a} Measured for MeCN solutions (0.010 mM) at 298 K.
Curiously, in the solid state and in acetonitrile solution, 90·PF₆ was strongly fluorescent, but none of the other complexes were fluorescent in the solid state, 85·Cl - 88·Cl, or 91 - 93·Cl were not fluorescent in methanol solution and 89·PF₆ was not fluorescent in acetonitrile solution. For 90·PF₆ in acetonitrile (Figure 6.16), luminescence emission spectrum (λₑₓ = 254 nm) shows four prominent emission bands, the strongest peak centred at 490 nm. The excitation spectrum (λₑˑm = 490 nm) displayed two peaks, with maxima at 210 and 254 nm, and resembled the electronic absorption spectrum. For the major emission at 490 nm with excitation at 254 nm, quantum yield (Φ) relative to quinine sulfate³⁰,³¹ is 0.76 and the brightness (Φ x ε / 1000) is 41.8. This brightness is in the range seen for green fluorescent proteins.³²

Figure 6.16 Room temperature electronic absorption (green), excitation (red) and emission (black; λₑˑx = 254 nm) spectra for the complex 90·PF₆ (0.10 mM in MeCN). Insets: Photos luminescence from (a) a solution of 90·PF₆ (0.10 mM in MeCN) in a quartz cuvette and (b) powdered 90·PF₆ in a silica sample vial.
It is interesting that of all the Au-IMT complexes examined, only \(90\cdot\text{PF}_6\) was luminescent. In the solid state, aurophilic interactions within cyclic cation trimers (Au···Au 3.0466(1) in \(90^+\), see Figure 6.6 above) are likely the source of emission. While some of the other Au-IMT complexes showed Au···Au contacts in the ~ 3 Å range, none had this cyclic trimeric structure in the solid state. In solution, it would be surprising if isolated cations \(90^+\) or even dimers \(90d^{2+}\) implicated in NMR and mass spectrometry studies of \(90\cdot\text{PF}_6\) (see above) were fluorescent, since neither are expected to have short Au···Au contacts. NOESY and ROESY \(^1\)H NMR studies of \(90\cdot\text{PF}_6\) in CD$_3$CN did not show any signals that could be attributed to correlations, such as between the CH$_3$ protons and H4 and H6 of the \(m\)-xylyl ring, which would be expected if the cyclic trimer was present.

### 6.7 Electrochemical studies

The redox properties of the gold complexes were studied by cyclic voltammetry of solutions in CH$_3$CN (Figure 6.17 and Table 6.6), using 0.1 M Bu$_4$NClO$_4$ as a supporting electrolyte, ferrocenium/ferrocene as an internal reference, a glassy carbon working electrode, and platinum counter and reference electrodes, at a scan rate of 400 mV/s. All complexes showed one reduction wave (A) and two oxidation waves (B and C). Wave A is presumably related to the reduction of Au$^+$ to Au$^0$ and the reverse process emerges at wave B. This type of quasi-reversibility has been observed at similar potentials for Au$^+$ NHC systems.$^{28,33}$ Wave C is tentatively attributed to the oxidative dissolution of deposited Au$^0$ on the electrode to Au$^+$ species.$^{28}$
Figure 6.17 Overlaid cyclic voltammograms of all Au\textsuperscript{i} complexes at 400 mV/s with 0.1 M Bu\textsubscript{4}NClO\textsubscript{4} as a supporting electrolyte.
Chapter 6: Au	extsuperscript{I} complexes of imidazole-2-thiones

| Table 6.6 | Cyclovoltammetric properties of the Au	extsuperscript{I}-IMT complexes $^a$ |
| Complexes | A (Au	extsuperscript{I} / Au	extsuperscript{0}) | B (Au	extsuperscript{0} / Au	extsuperscript{I}) | C (Au	extsubscript{ads} / Au	extsuperscript{I}) |
| 85·Cl    | - 1.13 | - 0.71 | 0.65 |
| 86·Cl    | - 1.15 | - 0.75 | 0.75 |
| 87·2Cl   | - 1.35 | - 0.83 | 0.52 |
| 88·2Cl   | - 1.22 | - 0.77 | 0.86 |
| 89·2PF$_6$ | - 1.28 | - 0.82 | 0.56 |
| 90·PF$_6$ | - 1.32 | - 0.74 | 0.69 |
| 93·Cl    | - 1.21 | - 0.63 | 0.96 |

$^a$ Measured in CH$_3$CN at a scan rate of 400 mV/s with 0.1 M Bu$_4$NClO$_4$, as a supporting electrolyte.
6.8 References


Chapter 7: Conclusions and future studies

7.1 \( \text{Au}^{\text{II}} \)-NHC and \( \text{Au}^{\text{I}}/\text{Au}^{\text{III}} \)-NHC complexes

When dinuclear \( \text{Au}_2(\text{NHC})_4 \) complexes are oxidised by \( \text{SOCl}_2 \), \( \text{Br}_2 \), or \( \text{I}_2 \), the outcome depends largely on structural constraints imposed by the NHC ligands. Amongst the cyclophane-bis(NHC) complexes studied in this work, when the bis(NHC) ligands impose short \( \text{Au} \cdots \text{Au} \) distances, as in salts of \( 11^{2+} \), oxidation leads to \( 34 \cdot 2\text{Cl}, 35 \cdot 2\text{Br}, \) and \( 36 \cdot 2\text{PF}_6 \), each containing an \( X \cdot \text{Au} \cdot \text{Au} \cdot X \) moiety in which both \( \text{Au} \) centres are formally \( \text{Au}^{\text{III}} \). When the cyclophane bis(NHC) ligand does not permit short \( \text{Au} \cdots \text{Au} \) distances but permits larger \( \text{Au} \cdots \text{Au} \) distances, as in \( 12 \cdot 2\text{Br} \), oxidation with \( \text{Cl}_2 \) or \( \text{Br}_2 \) resulted in products \( 37 \cdot 2\text{Cl} \) and \( 38 \cdot 2\text{Br} \), each containing unprecedented \( X \cdots \text{Au} \cdots X \cdots \text{Au} \) moieties, one \( \text{Au} \) centre being formally \( \text{Au}^{\text{III}} \), the other \( \text{Au}^{\text{I}} \).
Attempted oxidation of $12 \cdot 2PF_6$ with $I_2$ did not result in formation of stable products analogous to $37 \cdot 2Cl$ and $38 \cdot 2Br$. Presumably, the cyclophane ligands hold the Au centres too close together to permit insertion of $I^-$ in between (thus preventing formation of an $I−Au−I⋯Au$ moiety cf. Figure 7.1). Even with excess oxidising agents, there was no evidence for products containing two Au$^{III}$ centres.

![Figure 7.1](image_url)

In solution, interconversion of the Au$I$ and Au$^{III}$ sites within $37^{2+}$ and $38^{2+}$ occurred rapidly on the NMR timescale, which may offer interesting possibilities for catalysis involving Au in redox processes.

Further extensions in this project could explore oxidation of more highly functionalised structures, for example pyridinocyclophane Au$I$-NHC complexes (e.g. $97^{2+}$). The oxidation reaction in this case might be similar to oxidations of complexes $37^{2+}$ or $38^{2+}$, or it might be different, for example due to the potential of pyridine units in $97^{2+}$ coordinating with Au$^{III}$. The presence of pyridine units might also lead to additional opportunities for interesting catalytic activity. Further work to isolate
products of oxidation reactions of $39^{2+}$ and $40^+$ should also lead to interesting new Au-NHC cyclophane complexes.

7.2 \textbf{Au}^{III}-(\text{NHC})_4 \text{ complexes}

\text{Au}^{III} \text{ complexes of form } [\text{AuCl}_2(\text{diNHC})_2]\text{Cl (e.g., 45·Cl)} \text{ can be synthesized in good yield directly from bis- and tetrakis(imidazolium) salts and KAuCl}_4 \text{ in the presence of base. These formally 20 electron complexes have strongly distorted octahedral coordination of the Au}^{III} \text{ centre, the NHC groups making an approximately square planar array and the chlorido ligands occupying more distant axial positions. The Au}^{III}(\text{NHC})_4 \text{ motif is remarkably stable, resisting decomposition in DMSO solution at 120 °C or D}_2\text{O at 100 °C for extended periods. The axial (chlorido) ligands are labile, and metathesis of the } [\text{AuCl}_2(\text{diNHC})_2]\text{Cl salts with KPF}_6 \text{ in methanol/water results in}
removal of the chlorido ligands and formation of three new, formally 16 electron complexes of form \([\text{Au(NHC)}_4](\text{PF}_6)_3\) (e.g., \(48 \cdot 3\text{PF}_6\)). The \([\text{Au(NHC)}_4]^{3+}\) ion is sufficiently stable to undergo base-catalysed H/D exchange reactions at most sites on the NHC ligands in D\(_2\)O at 100 °C without evidence of decomposition.

Further work could involve exploration of a propylene-linked diazolium salt would give similar results for the gold(III) system. In addition, it would be interesting to explore reactions of other bis(NHC) precursors, such as the ortho-cyclophane \(30 \cdot 2\text{HCl}\) or the pyridinocyclphane \(98 \cdot 2\text{HCl}\) (Scheme 7.1). Complex \(99 \cdot 3\text{Cl}\) is an interesting target as it is an Au\(^{\text{III}}\) analog of \([\text{Au}^\text{I}(\text{DPPE})_2]^+\), a well-known anti-mitochondrial agent.\(^1\) Complex \(100 \cdot 3\text{Cl}\) is an analog of an interesting saddle-shaped Ni\(^{\text{II}}\)-NHC complex.\(^4\)
Scheme 7.1

7.3 \( \text{Au}^{\text{III}} \)-NHC complexes bearing cyanido ligands

New \( \text{Au}^{\text{III}} \)-NHC complexes containing cyanido ligands can be synthesized by treatment of precursors of form \([\text{Au}^{\text{III}}X_2\{\text{bis-NHC}\}_2]_2X_2\) with NaCN. Most of these complexes are mononuclear and contain the unprecedented \( \text{cis-Au}^{\text{III}}\text{CN}_2(\text{NHC})_2 \) motif (e.g., 63·Br), while others are dinuclear and contain \( \text{trans-Au}^{\text{III}}\text{CN}_2(\text{NHC})_2 \) cores (e.g., 70·2Br). For the complexes containing the \( \text{cis-Au}^{\text{III}}\text{CN}_2(\text{NHC})_2 \) motif, the two NHC units and two cyanido ligands comprise an approximate square planar array around the \( \text{Au}^{\text{III}} \) centre, and the two NHC units are mutually \( \text{cis} \). The conformations of these complexes in solution are consistent with those seen in the solid state, except that in the
case of 67·Au(CN)₄. For 67·Au(CN)₄ there are two conformations: a syn conformation similar to that seen in the solid state, and an anti conformation formed slowly in solution and detected by ¹H NMR spectroscopy.

Potential further work could involve exploration of ligand exchange reactions in cyclophane complexes (e.g. 35·2Br or 38·2Br, Chapter 2). For example, treatment of the dinuclear Au⁺⁻⁻-NHC complex 35·2Br with NaCN may lead to new complexes such as the dinuclear Au⁺⁻⁻-NHC complex 101·2Br, or disproportionation may occur to yield an Au⁺ complex and an Au⁺⁺ complex such as 102·Br (Scheme 7.2).
Since many Au$^{III}$-NHC complexes have shown interesting catalytic activities,$^{5-8}$ it would be worthwhile to expand these studies to explore catalysis properties of the new Au$^{III}$(NHC)$_2$CN$_2$ complexes.

### 7.4 Imidazole-2-thiones and their Au$^1$-IMT complexes

New cyclophanes containing IMT moieties (e.g., 31 and 33) have been synthesized by the reaction of cyclophane bis(NHC)s with sulfur. The conformational behaviour of these cyclophane-IMT compounds has characterized by NMR and X-ray diffraction methods.
Further work could explore routes to other interesting cyclophane-IMT ligands (e.g., 103), or reactions of sulfur with more complex imidazolium systems, such as the triply-bridged cyclophane 104·3HBr.

New AuI-IMT complexes (e.g., 85·Cl, 87·2Cl, 91 and 93·Cl) were synthesized directly from Au(SMe2)Cl and the appropriate IMT ligands. The structures and conformations of these new complexes were characterized using X-ray diffraction and NMR studies.
X-Ray studies of these complexes showed that the IMT ligands provide an essentially linear coordination array around the Au\(^1\) centres with the C=S bonds roughly orthogonal to the S-Au-S axis. Many of the new Au-IMT complexes form cation dimers and trimers in the solid state, via Au···Au interactions, and more extensive supramolecular interactions via hydrogen bonding. However, NMR studies showed that, in solution, most of the new Au\(^1\)-IMT complexes are conformationally labile and, while some of the complexes are dinuclear, there is no evidence for aggregation via Au···Au interactions. In two particularly interesting cases, there appeared to be an equilibrium between a mononuclear complex (e.g., 90\(^+\)) and a dinuclear complex (e.g., 90d\(^{2+}\)) in solution, undergoing exchange reactions rapidly on the NMR timescale.

The investigation of Au\(^1\)-IMT complexes as potential anticancer agents should be explored. Thus, study of their reactions with biologically relevant molecules (e.g., histidine and cysteine) would be worthwhile, as would cell studies to assay anticancer activity and selectivity.
7.5 References

Chapter 8: Experimental

8.1 General procedures

Nuclear magnetic resonance spectra were recorded using Bruker ARX400 (400.13 MHz for $^1$H), Bruker ARX500 (500.13 MHz for $^1$H and 125.77 MHz for $^{13}$C), or Bruker ARX 600 (600.13 MHz for $^1$H, 150.90 MHz for $^{13}$C and 242.94 MHz for $^{31}$P) spectrometers at ambient temperature unless otherwise indicated. $^1$H and $^{13}$C NMR chemical shifts were referenced to residual signal of the solvent (DMSO-$d_6$: $^1$H 2.50 ppm; $^{13}$C 39.52 ppm, CD$_3$CN: $^1$H 1.94 ppm; $^{13}$C 1.32, 118.26 ppm, methanol-$d_4$: $^1$H 3.31 ppm; $^{13}$C 49.00 ppm, D$_2$O: $^1$H 4.79 ppm)$^1$, and $^{31}$P chemical shifts were referenced to an external 85 % H$_3$PO$_4$ solution. When necessary, $^1$H-$^{13}$C HSQC (heteronuclear single quantum coherence) and $^1$H-$^{13}$C HMBC (heteronuclear multiple bond correlation) spectra were used to assign signals. Conductance measurements were performed by using a TPS Aqua-CP/A conductivity meter. Cyclic voltammetry experiments were recorded using an eDAQ e-corder 401 system in a three-electrode cell with a glassy carbon (1 mm diameter) working electrode, a platinum (1 mm diameter) counter electrode, and a platinum wire reference electrode. Measurements were taken at room temperature (25 °C) in acetonitrile with 0.1 M Bu$_4$NClO$_4$ as a supporting electrolyte. Microanalyses were performed by The School of Chemistry & Molecular Bioscience, University of Queensland, Australia, and the Instrument Center of National Chung Hsing University, Taiwan. High resolution mass spectra were measured using Agilent LCMS 6510 Q-TOF or Waters LCT Premier XE spectrometers, using the ESI or APCI method, with CH$_3$CN:H$_2$O (9:1) as solvent. X-Ray structures were solved and refined by Prof. Brian W. Skelton and Prof. Alexandre N. Sobolev. All organometallic compounds were prepared under a nitrogen atmosphere.
8.2 Materials

8.2.1 General reagents
The following compounds were used as received: 37 % hydrochloric acid (Emsure), 69% nitric acid (Emsure), sodium hydroxide (Unilab, AR), sodium tetrafluoroborate (Unilab, AR), sodium cyanide (BDH), potassium carbonate (Univar, AR), imidazole (Fluka), 1,2-dichloroethane (Fluka), thionyl chloride (Riedel de Haen), potassium hexafluorophosphate (Aldrich, 98%), 1-methylimidazole (Aldrich), 2-bromopropane (Aldrich), diiodomethane, 1,2-dibromoethane (Aldrich), 1,2-bis(chloromethyl)benzene (Aldrich), 1,2-bis(bromomethyl)benzene (Aldrich), 1,3-bis(chloromethyl)benzene (Aldrich), 1,3-bis(bromomethyl)benzene (Aldrich), 2,4-bis(bromomethyl)mesitylene (Aldrich), 2,6-dibromopyridine (Aldrich), sulfur (BDH), tetramethylammonium bromide (BDH), tetrabutylammonium perchlorate (Fluka), tetraethylammonium chloride (BDH), silver hexafluorophosphate (Ozark), potassium iodide (William), sodium chloride (Emsure), sodium bromide (BDH), iodine (Evans), bromine (BDH).

8.2.2 Organometallic reagents

Au(SMe$_2$)Cl and Au(SMe$_2$)Br were prepared using literature methods. KAuCl$_4$ was prepared using modification of literature method. KAuCl$_4$ was synthesized by dissolving Au (0.83 g, 4.17 mmol) in aqua regia (13 mL of HCl and 2 mL of HNO$_3$). The solution was cooled at room temperature and allowed to evaporate HNO$_3$. K$_2$CO$_3$ (0.28 g, 2.03 mmol) was added, the solvent was removed under nitrogen, and the residue was recrystallized from acetonitrile to give KAuCl$_4$ as yellow crystals (1.5 g, 93%).
8.3 Preparation of compounds

8.3.1 Imidazolium salts

1,3-Dimethylimidazolium iodide

\[ \text{N} \quad \text{N} \quad \text{I}^{-} \]

1-Methimidazole (1 mL, 12.2 mmol) and iodomethane (1.35 mL, 14.6 mmol) were dissolved in THF (15 mL) and refluxed for 48 hours. The precipitated solid was washed three times with THF to give white solid (2 g, 73%).

\(^1\text{H NMR (500 MHz, DMSO-}d_{6}\text{): } \delta 9.11 \text{ (s, 1H, H2), 7.71 (s, 2H, H4/H5), 3.85 (s, 6H, 2} \times \text{CH}_3\).}

NMR data are consistent with literature values.\(^4\)

1-Ethyl-3-methylimidazolium bromide

\[ \text{N} \quad \text{N} \quad \text{Br}^{-}\]

1-Methimidazole (5 mL, 61 mmol) and bromoethane (10 mL, 130 mL) were refluxed for 16 hours. The mixture was then cooled to room temperature and the resulting white precipitate was collected by filtration and recrystallized from methanol to give the product as colourless crystals (7.5 g, 65%).
$^1$H NMR (500 MHz, CDCl$_3$): $\delta$ 10.43 (s, 1H, H2), 7.52 (d, $^3J_{H,H} = 2.4$ Hz, 1H, H4/H5), 7.50 (d, $^3J_{H,H} = 2.4$ Hz, 1H, H4/H5), 4.40 (q, $^3J_{H,H} = 7.4$ Hz, 2H, H2') 4.10 (s, 3H, H3'), 1.60 (t, $^3J_{H,H} = 7.4$ Hz, 3H, H1').

NMR data are consistent with literature values.$^5$

1-Isopropylimidazole$^6$

\[
\begin{align*}
\text{N} & \quad 2' \\
& \quad \text{N} \\
& \quad 4 \\
& \quad 5 \\
& \quad 2
\end{align*}
\]

Sodium hydroxide (1.19 g, 30 mmol), was added to a solution of imidazole (1.36 g, 20 mmol) in DMSO (10 mL), the mixture was stirred for 30 min at room temperature. The reaction was cooled to 0°C and 2-bromopropane (1.9 mL, 20 mmol) was added dropwise over 10 min and then the mixture was allowed to warm to room temperature over 2 h. The mixture was diluted with water (100 mL) and extracted with CH$_2$Cl$_2$ (5 × 10 mL). The organic extracts were combined and the solvent was removed under vacuum, to leave the product as a colourless liquid (1.73 g, 78.5%).

$^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 7.43 (s, 1H, H2), 6.95 (s, 1H, H4/H5), 6.86 (s, 1H, H4/H5), 4.24 (sept., $^3J_{H,H} = 6.0$ Hz, 1H, H1'), 1.37 (d, $^3J_{H,H} = 2.0$ Hz, 6H, H2').

NMR data are consistent with literature values.$^6$
1,3-Diisopropylimidazolium bromide

\[
\begin{array}{c}
\text{Br} \\
\text{N}^+ \quad \text{N}^+ \\
\text{2} \quad \text{1'}
\end{array}
\]

1-Isopropylimidazole (1.32 g, 12 mmol) and 2-bromopropane (13.5 mL, 144 mmol) were combined and the mixture was refluxed overnight. The mixture was cooled to room temperature and the product was filtered off and washed with Et₂O (3 × 10 mL) and dried under vacuum to leave the product as a white crystalline solid (2.54 g, 91%).

\(^1\)H NMR (600 MHz, DMSO-d\(_6\)): δ 9.36 (s, 1H, H2), 7.94 (d, \(^3\)J\(_{H,H}\) = 1.2 Hz, 2H, H4/H5), 4.62 (sept., \(^3\)J\(_{H,H}\) = 13.2 Hz, 2H, H1'), 1.48 (d, \(^3\)J\(_{H,H}\) = 7.2 Hz, 12H, H2').

\(^{13}\)C NMR (150.90 MHz, DMSO-d\(_6\)): δ 133.56 (C2), 120.66 (C4/C5), 52.24 (C1'), 22.34 (C2').

NMR data are consistent with literature values.\(^6\)

1,1'-Methylene bis(3-methylimidazolium) dichloride 42·2HCl

\[
\begin{array}{c}
\text{2Cl}^- \\
\text{N}^+ \quad \text{N}^+ \\
\text{2} \quad \text{1'}
\end{array}
\]

A mixture of 1-methylimidazole (1.0 g, 1 mL, 12.2 mmol) and dichloromethane (25 mL, 391.5 mmol) was stirred in a Schlenk flask for 48 h at 100 °C. The resulting white precipitate was filtered off, washed with Et₂O (3 × 10 mL), and dried in vacuo (1.42 g, 47%).
\(^1\text{H NMR}\ (600 \text{ MHz, DMSO-}\text{d}_6): \delta \ 9.82 \ (s, 2\text{H}, \text{H2}), \ 8.23 \ (s, 2\text{H}, \text{H4/H5}), \ 7.80 \ (s, 2\text{H}, \text{H4/H5}), \ 6.88 \ (s, 2\text{H}, \text{CH}_2), \ 3.89 \ (s, 6\text{H}, \text{CH}_3)\).

\(^{13}\text{C NMR}\ (150.90 \text{ MHz, DMSO-}\text{d}_6): \delta \ 138.20(\text{C2}), \ 124.19 \ (\text{C4/C5}), \ 122.05 \ (\text{C4/C5}), \ 57.59 \ (\text{C1'})\), \ 36.21 \ (\text{C2'})\).

NMR data are consistent with literature values.\(^7\)

**1,1'-Methylene bis(3-methylimidazolium) diiodide 42-2HI \(^8\)**

\[
\begin{align*}
2^{-} & \\
\text{N} & \text{N} \\
4 & 5
\end{align*}
\]

A mixture of 1-methylimidazole (0.5 g, 0.5 mL, 6.5 mmol) and diiodomethane (0.80 g, 0.25 mL, 3 mmol) was dissolved in THF (2 mL) in a thick-walled flask sealed with a Young's tap. The mixture was stirred for 3 h at 110 °C until a white precipitate was formed. The solid was filtered off and washed with THF (5 mL) and toluene (5 mL), then dried *in vacuo* to give the product as a white powder (1.54 g, 86%).

\(^1\text{H NMR}\ (500 \text{ MHz, DMSO-}\text{d}_6): \delta \ 9.33 \ (s, 2\text{H}, \text{H2}), \ 7.78-7.79 \ (d, \ ^3\text{J}_{H,H} = 2.0 \text{ Hz, 2H, H4/H5}), \ 7.93-7.94 \ (d, \ ^3\text{J}_{H,H} = 2.0 \text{ Hz, 2H, H4/H5}), \ 6.62 \ (s, 2\text{H}, \text{CH}_2), \ 3.89 \ (s, 6\text{H}, \text{CH}_3)\).

NMR data are consistent with literature values.\(^8\)
1-(2'-chloroethyl)-3-methylimidazolium chloride

1-Methylimidazole (2 g, 2 mL, 25 mmol) was added to 1,2-dichloroethane (25 g, 20 mL, 252 mmol) and the mixture was stirred at reflux for 16 h. An oily residue formed over the course of the reaction. The residue was dissolved with CH$_3$CN (2 × 20 mL) and Et$_2$O (30 mL) was added, oiling out the hygroscopic product. The solution was poured off and the oily residue was washed with Et$_2$O (2 × 10 ml) and dried in vacuo to give the product as colourless hygroscopic oil (3 g, 66%).

$^1$H NMR (600 MHz, DMSO-$d_6$): $\delta$ 9.24 (s, 1H, H2), 7.84-7.83 (d, $^3$J$_{H,H}$ = 1.8 Hz, 1H, H4/H5), 7.76-7.75 (d, $^3$J$_{H,H}$ = 1.8 Hz, 1H, H4/H5), 4.56 (t, $^3$J$_{H,H}$ = 0.6 Hz, 2H, H2'), 4.08 (t, $^3$J$_{H,H}$ = 0.6 Hz, 2H, H1'), 3.89 (s, 3H, H1'').

NMR data are consistent with literature values.$^9$

1,1'-Ethylene bis(3-methylimidazolium) dichloride 43·2HCl

A mixture of 1-methylimidazole (1 g, 1 mL, 12.5 mmol) and 1-(2'-chloroethyl)-3-methylimidazolium chloride (2.3 g, 12.5 mmol) in CH$_3$CN (25 mL) was stirred at 100 °C overnight. The precipitate that formed was collected by filtration washed once with CH$_3$CN and Et$_2$O several times to give the product as colourless crystals (2.2 g, 67%).
$^1$H NMR (600 MHz, DMSO-$d_6$): $\delta$ 9.37 (s, 2H, H2), 7.73-7.72 (d, $^3$J$_{H,H}$ = 1.8 Hz, 4H, H4/H5), 4.75 (s, 4H, CH$_2$CH$_2$), 3.85 (s, 6H, CH$_3$).

NMR data are consistent with literature values.$^{10}$

1,1'-Methylene bis(imidazole)

![Diagram of 1,1'-Methylene bis(imidazole)]

Potassium hydroxide (5 g, 88 mmol) was added to a solution of imidazole (3 g, 44 mmol) in dichloromethane (100 mL) and the mixture was refluxed for overnight. The solvent was decanted and volatiles were removed to leave a white solid, which was washed with ether and dried to give 1,1'-methylene bis(imidazole) as a white powder (3.8 g, 60%).

$^1$H NMR (600 MHz, DMSO-$d_6$): $\delta$ 7.92 (s, 2H, H2), 7.38 (s, 2H, H4/H5), 6.9 (s, 2H, H4/H5), 6.2 (s, 2H, CH$_2$).

NMR data are consistent with literature values.$^{11}$
The *ortho*-cyclophane tetra-imidazolium chloride salt 44·4HCl

\[
\begin{align*}
\text{N} & \text{N} \\
\text{N} & \text{N} \\
\text{N} & \text{N} \\
\end{align*}
\]

Separate solutions of 1,1'-methylene bis(imidazole) (0.3 g, 2 mmol) in CH$_3$CN (25 mL) and a solution of α,α'-dichloro-o-xylene (0.35 g, 2 mmol) in CH$_3$CN (25 mL) were added dropwise to CH$_3$CN (150 mL) over 1 hour and the mixture was refluxed for 72 h. After that, the mixture was filtered and the precipitate was washed with CH$_3$CN and recrystallized from methanol to give white powder (0.11 g, 10%).

$^1$H NMR (600 MHz, DMSO-$d_6$): δ 9.29 (s, 4H, H2), 8.02 (br s, 4H, H4/H5), 7.74 (br s, 4H, H4/H5), 7.55 (m, 4H, H3'/H6'), 7.30 (m, 4H, H4'/H5'), 6.68 (s, 4H, 2 × CH$_2$), 5.50 (s, 8H, 4 × benzylic CH$_2$).

NMR data are consistent with literature values.$^{12}$

The *ortho*-cyclophane tetra-imidazolium bromide salt 44·4HBr

\[
\begin{align*}
\text{N} & \text{N} \\
\text{N} & \text{N} \\
\text{N} & \text{N} \\
\end{align*}
\]

Separate solutions of 1,1'-methylene bis(imidazole) (0.2 g, 1 mmol) in CH$_3$CN (25 mL) and α,α'-dibromo-o-xylene (0.3 g, 1 mmol) in CH$_3$CN (25 mL) were added dropwise to
CH$_3$CN (150 mL) over 1 hour and the mixture was refluxed for 48 h. After that, the mixture was filtered and the precipitate was washed with CH$_3$CN and recrystallized from methanol to give the product as white powder (0.2 g, 20%).

$^1$H NMR (600 MHz, DMSO-$d_6$): $\delta$ 9.51 (s, 4H, H$_2$), 8.06 (br s, 4H, H$_4$/H$_5$), 7.76 (br s, 4H, H$_4$/H$_5$), 7.53 (m, 4H, H$_3'$/H$_6'$), 7.35 (m, 4H, H$_4'/H_5'$), 6.76 (s, 4H, 2 $\times$ CH$_2$), 5.59 (s, 8H, 4 $\times$ benzylic CH$_2$).

NMR data are consistent with literature values.$^{12}$

**1,1'-(o-Xylylene)bis(3-methylimidazolium chloride)**

A solution of $\alpha, \alpha'$-dichloro-o-xylene (0.5 g, 3 mmol) in THF (20 mL) was added to 1-methylimidazol (0.5 g, 0.5 mL, 6.3 mmol). The reaction mixture was then refluxed overnight. After that, a white powder product was filtered, washed with ether and dried in vacuo, and then recrystallisation from CH$_3$CN to give (0.4 g, 37%).

$^1$H NMR (400 MHz, DMSO-$d_6$): $\delta$ 9.25 (s, 2H, H$_2$), 7.75-7.74 (d, $^3$J$_{H,H} = 6.8$ Hz, 4H, H$_4$/H$_5$), 7.49-7.47 (m, 2H, H$_4'/H_5'$), 7.33-7.31 (m, 2H, H$_3'/H_6'$), 5.62 (s, 4H, 2 $\times$ benzylic CH$_2$), 3.86 (s, 6H, 2 $\times$ CH$_3$).

NMR data are consistent with literature values.$^{13}$
1,1'-(o-Xylylene)bis(3-methylimidazolium bromide)

1-Methylimidazole (0.8 g, 0.75 mL, 9.5 mmol) was added to a stirred solution of α,α'-dibromo-o-xylene (1 g, 4 mmol) in 1,4-dioxane (13 mL). This mixture was heated to 100 °C overnight. The precipitate which formed was collected, washed with Et₂O and dried in vacuo to give the product as colourless crystals (1.5 g, 86 %).

\( ^1H \) NMR (600 MHz, DMSO-\( d_6 \)): \( \delta 9.12 \) (s, 2H, H2), 7.76-7.70 (d, \( ^3J_{H,H} = 36 \) Hz, 4H, H4/H5), 7.49-7.48 (m, 2H, H4'/H5'), 7.23-7.30 (m, 2H, H3'/H6'), 5.58 (s, 4H, 2 × benzylic CH₂), 3.86 (s, 6H, 2 × CH₃).

NMR data are consistent with literature values.

1,1'-(m-Xylylene)bis(3-methylimidazolium chloride)
A solution of α,α'-dichloro-m-xylene (0.55 g, 3.2 mmol) in acetone (20 mL) was added to 1-methylimidazole (0.5 g, 0.5 mL, 6.3 mmol) in acetone (20 mL). The reaction mixture was then refluxed overnight. After that, a white powder product was filtered, washed with acetone and dried in vacuo, and then recrystallisation from CH$_3$CN to give (0.9 g, 86%).

$^1$H NMR (600 MHz, DMSO-$d_6$): δ 9.34 (s, 2H, H2), 7.79 (d, $^3$J$_{HH}$ = 2 Hz, 2H, H4/H5), 7.73 (d, $^3$J$_{HH}$ = 2 Hz, 2H, H4/H5), 7.41 (d, $^3$J$_{HH}$ = 7.8 Hz, 2H, H4'/H6'), 7.47 (t, $^3$J$_{HH}$ = 7.8 Hz, 1H, H5'), 7.54 (s, 1H, H2'), 5.43 (s, 4H, 2 × benzylic CH$_2$), 3.86 (s, 6H, 2 × CH$_3$).

NMR data are consistent with literature values.$^{14}$

1,1'-(m-Xylene)bis(3-methylimidazolium bromide)

A solution of α,α'-dibromo-m-xylene (0.79 g, 3 mmol) in acetone (20 mL) was added to 1-methylimidazol (0.5 g, 0.5 mL, 6.3 mmol) in acetone (20 mL). The reaction mixture was then refluxed overnight. After that, a white powder product was filtered, washed with acetone and dried in vacuo, and then recrystallisation from CH$_3$CN to give (0.7 g, 87%).
$^1$H NMR (600 MHz, DMSO-$d_6$): $\delta$ 9.39 (s, 2H, H2), 7.84 (d, $^3$J$_{H,H} = 2$ Hz, 2H, H4/H5), 7.75 (d, $^3$J$_{H,H} = 2$ Hz, 2H, H4/H5), 7.44 (d, $^3$J$_{H,H} = 7.8$ Hz, 2H, H4'/H6'), 7.49 (t, $^3$J$_{H,H} = 7.8$ Hz, 1H, H5'), 7.60 (s, 1H, H2'), 5.49 (s, 4H, 2 × benzylic CH$_2$), 3.90 (s, 6H, 2 × CH$_3$).

NMR data are consistent with literature values.$^{14}$

**1,2-Bis(imidazol-1-ylmethyl)benzene$^{13}$**

A solution of imidazole (5.4 g, 79 mmol) and α,α'-dichloro-o-xylene (0.9 g, 5 mmol) in methanol (250 mL) was refluxed for 48 h. The solvent was removed under reduced pressure and the resulting residue was added to an aqueous solution of K$_2$CO$_3$ (6%, 50 mL), and the solution allowed to stand overnight. The white solid that precipitated was collected and recrystallised from methanol to give colourless crystals (0.8 g, 65%).

$^1$H NMR (400 MHz, DMSO-$d_6$): $\delta$ 7.66 (s, 2H, H2), 7.25-7.27 (m, 2H, H3'/H6'), 7.04-7.05 (m, 4H, H4/H5), 6.90-6.93 (m, 2H, H4'/H5'), 5.28 (s, 4H, 2 × benzylic CH$_2$).

NMR data are consistent with literature values.$^{13}$
The *o*-cyclophane dichloride salt 30·2HCl\textsuperscript{13}

A solution of α,α'-dichloro-*o*-xylene (0.6 g, 3.4 mmol) in acetone (50 mL) was added dropwise to a solution of 1,2-bis(imidazolylmethyl)benzene (0.81 g, 3.40 mmol) in acetone (50 mL) at room temperature and refluxed for 72 h. The precipitated *o*-cyclophane salt (0.5 g, 36%) was collected by filtration and used without further purification.

\textsuperscript{1}H NMR (600 MHz, DMSO-\textit{d}_6): δ 8.65 (br s, 2H, H2), 7.81 (m, 4H, H3'/H6'), 7.68 (m, 4H, H4'/H5'), 7.47 (br s, 4H, H4/H5), 5.55 (br s, 8H, 4 × benzylic CH\textsubscript{2}).

NMR data are consistent with literature values.\textsuperscript{13}

The *o*-cyclophane dibromide salt 30·2HBr\textsuperscript{13}

A solution of α,α'-dibromo-*o*-xylene (0.9 g, 3.4 mmol) in acetone (50 mL) was added dropwise to a solution of 1,2-bis(imidazolylmethyl)benzene (0.8 g, 3.4 mmol) in acetone (50 mL) at room temperature and the mixture was refluxed for 48 h. The
precipitated \( o \)-cyclophane dibromide salt (1.4 g, 75 \%) was collected by filtration and used without further purification.

\[^1\text{H} \text{NMR} \ (600 \text{ MHz}, \text{ DMSO-}d_6): \delta \ 8.30 \text{ (br s, 2H, H2)}, 7.83 \text{ (m, 4H, H3'/H6')}, 7.70 \text{ (m, 4H, H4'/H5')}, 7.17 \text{ (br s, 4H, H4/H5)}, 5.60 \text{ (br s, 8H, 4 \times \text{ benzylic CH}_2)}.\]

NMR data are consistent with literature values.\(^{13}\)

**1,3-Bis(imidazol-1-ylmethyl)benzene\(^{15}\)**

A solution of \( \alpha,\alpha' \)-dibromo-\( m \)-xyylene (1.5 g, 5.5 mmol) and imidazole (4 g, 59.5 mmol) in methanol (70 mL) was refluxed for 48 h. The solvent was removed under reduced pressure and aqueous 6\% w/v \( \text{K}_2\text{CO}_3 \) solution (50 mL) was added to the residue. The solution was allowed to stand overnight. The product separated as colourless crystals (0.7 g, 53 \%) that were collected by filtration.

\[^1\text{H} \text{NMR} \ (500 \text{ MHz}, \text{ DMSO-}d_6): \delta \ 7.72 \text{ (s, 2H, H2)}, 7.33 \text{ (t, } ^3\text{J}_{\text{H,H}} = 7.5 \text{ Hz, 1H, H5'}), 7.19 \text{ (s, 1H, H2')}, 7.15 \text{ (m, 4H, H4/H5)}, 6.89 \text{ (d, } ^3\text{J}_{\text{H,H}} = 2.4 \text{ Hz, 2H, H4'/H6'}), 5.17 \text{ (s, 4H, 2 \times \text{ benzylic CH}_2)}.\]

NMR data are consistent with literature values.\(^{15}\)
The \textit{m}-cyclophane dichloride salt 32·2HCl$^{13,15}$

A solution of \(\alpha,\alpha'\)-chloro-\textit{m}-xylene (0.6 g, 3.4 mmol) in acetone (25 mL) was added dropwise to a solution of 1,3-bis(imidazol-1-ylmethyl)benzene (0.8 g, 3.4 mmol) in acetone (25 mL) and the mixture was refluxed for 72 h. The precipitated \textit{m}-cyclophane salt (0.7 g, 50\%) was collected by filtration and used without further purification.

\(^1\)H NMR (600 MHz, DMSO-\(d_6\)): \(\delta\) 9.75 (s, 2H, H2), 7.83 (s, 4H, H4/H5), 7.59-7.58 (d, \(^3\)J\(H,H\) = 7.8 Hz, 4H, H4'/H6'), 7.49-7.47 (t, \(^3\)J\(H,H\) = 7.8 Hz, 2H, H5'), 7.31 (s, 2H, H2'), 5.43 (s, 8H, 4 \times\) benzylic CH\(_2\)).

NMR data are consistent with literature values.$^{13,15}$

The \textit{m}-cyclophane dibromide salt 32·2HBr$^{13,15}$

A solution of \(\alpha,\alpha'\)-bromo-\textit{m}-xylene (0.6 g, 2.3 mmol) in acetone (25 mL) was added dropwise to a solution of 1,3-bis(imidazol-1-ylmethyl)benzene (0.5 g, 2.3 mmol) in acetone (25 mL), and the mixture was refluxed for 48 h. The precipitated meta-
cyclophane salt (0.8 g, 70%) was collected by filtration and used without further purification.

$^1$H NMR (600 MHz, DMSO-$_d_6$): $\delta$ 9.35 (s, 2H, H2), 7.82 (s, 4H, H4/H5), 7.58-7.57 (d, $^3$J$_{H,H}$ = 8.4 Hz, 4H, H4'/H6'), 7.52-7.51 (t, $^3$J$_{H,H}$ = 8.4 Hz, 2H, H5'), 7.02 (s, 2H, H2'), 5.44 (s, 8H, 4 $\times$ benzylic CH2).

NMR data are consistent with literature values.$^{13,15}$

**1,3-Bis(imidazol-1-ylmethyl)mesitylene**$^{15}$

A solution of 1,3-bis(bromomethyl)mesitylene (1.7 g, 5.5 mmol) and imidazole (3.7 g, 55 mmol) was refluxed in methanol (70 mL) for 24 h. The solvent was removed under reduced pressure and the resulting residue was added to an aqueous K$_2$CO$_3$ solution (6%, 70 mL). The solution was allowed to stand overnight and the resulting colourless crystals (1.1 g, 71%) were collected by filtration.

$^1$H NMR (500 MHz, DMSO-$_d_6$): 7.47 (s, 2H, H2) 7.03 (s, 1H, H5'), 6.87-6.84 (d, $^3$J$_{H,H}$ = 11.5 Hz, 4H, H4/H5), 5.20 (s, 4H, 2 $\times$ benzylic CH2), 2.27 (s, 6H, H$_a$), 2.19 (s, 3H, H$_b$).

NMR data are consistent with literature values.$^{15}$
The mesityleno-cyclophane salt 77·2HBr

A solution of 1,3-bis(imidazol-1-ylmethyl)mesitylene (1 g, 3.5 mmol) in acetone (25 mL) was added dropwise to a solution of 1,3-bis(bromomethyl)mesitylene (1.1 g, 3.5 mmol) in acetone (25 mL), and the mixture was refluxed for 48 h. The mesityleno-cyclophane salt precipitated as colourless crystals (1.8 g, 88%) that were collected by filtration and used without further purification.

$^1$H NMR (600 MHz, DMSO-d$_6$): $\delta$ 8.02 (s, 4H, H4/H5), 7.22 (s, 2H, H2), 7.11 (s, 2H, H5'), 5.48-5.45 (d, $^2$J$_{H,H}$ = 15.6 Hz, benzylic HCH), 5.35-5.32 (d, $^2$J$_{H,H}$ = 15 Hz, benzylic HCH), 2.35 (s, 12H, Ha), 1.54 (s, 6H, Hb).

NMR data are consistent with literature values.$^{15}$
8.3.2 Imidazole-2-thione

1,3-Dimethylimidazole-2-thione 78

\[
\begin{array}{c}
\text{N} \\
\text{N} \\
\text{S}
\end{array}
\]

A solution of 1,3-dimethylimidazolium iodide (450 mg, 2 mmol) in CH\textsubscript{3}OH (10 mL) was added to a mixture of sulfur (64 mg, 2 mmol) and K\textsubscript{2}CO\textsubscript{3} (330 mg, 2.4 mmol) in CH\textsubscript{3}OH (15 mL). The mixture was stirred for 48 h at room temperature. After that, the methanol was removed with a rotary evaporator. The residual powder was extracted by shaking with CH\textsubscript{2}Cl\textsubscript{2} (30 mL) followed by filtration, and this process was repeated twice more. The CH\textsubscript{2}Cl\textsubscript{2} extracts were combined and stripped of solvent (rotary evaporator) and the residue was recrystallised from CH\textsubscript{2}Cl\textsubscript{2}/CH\textsubscript{3}OH to give the product as a white crystalline solid (120 mg, 47%).

\textsuperscript{1}H NMR (500 MHz, d\textsubscript{4}methanol): \(\delta\) 6.99 (s, 2H, H4/H5), 3.55 (s, 6H, 2 \times \text{CH}_3).

NMR data are consistent with literature values.\textsuperscript{16}

1-Ethyl-3-methylimidazole-2-thione 82

\[
\begin{array}{c}
\text{N} \\
\text{N} \\
\text{S}
\end{array}
\]

A solution of 1-ethyl-3-methylimidazolium bromide (2.74 g, 14 mmol) in CH\textsubscript{3}OH (10 mL) was added to a mixture of sulfur (0.44 g, 14 mmol) and K\textsubscript{2}CO\textsubscript{3} (2.42 g, 17.5 mmol)
in CH$_3$OH (20 mL). The mixture was stirred for 40 h at room temperature. After that, the methanol was removed with a rotary evaporator. The residual powder was extracted by shaking with CH$_2$Cl$_2$ (30 mL) followed by filtration, and this process was repeated twice more. The CH$_2$Cl$_2$ extracts were combined and stripped of solvent (rotary evaporator) and the residue was recrystallised from CH$_2$Cl$_2$/CH$_3$OH to give the product as a white crystalline solid (1.5 g, 48%).

$^1$H NMR (500 MHz, DMSO-$d_6$): $\delta$ 7.1 (d, $^3J_{H,H} = 2.4$ Hz, 1H, H4/H5), 7.15 (d, $^3J_{H,H} = 2.4$ Hz, 1H, H4/H5), 3.95 (q, $^3J_{H,H} = 7.2$ Hz, 2H, H2') 3.45 (s, 3H, H3'), 1.2 (t, $^3J_{H,H} = 7.2$ Hz, 3H, H1').

NMR data are consistent with literature values.$^{17}$

1,1'-Methylenebis(3-methylimidazole-2-thione) 83

![Chemical Structure](image)

A solution of 42·2HI (0.25 g, 0.6 mmol) in CH$_3$OH (10 mL) was added to a mixture of sulfur (0.04 g, 1.2 mmol) and K$_2$CO$_3$ (0.2 g, 1.4 mmol) in CH$_3$OH (15 mL). The mixture was stirred for overnight at room temperature. After that, the methanol was removed with a rotary evaporator. The residual powder was extracted by shaking with CH$_2$Cl$_2$ (30 mL) followed by filtration, and this process was repeated twice more. The CH$_2$Cl$_2$ extracts were combined and stripped of solvent (rotary evaporator) and the residue was
recrystallised from CH₂Cl₂/CH₃OH to give the product as a white crystalline solid (0.1 g, 69%).

¹H NMR (600 MHz, DMSO-d₆): δ 7.39 (d, 3J_H,H = 2.4 Hz, 2H, H₄/H₅), 7.12 (d, 3J_H,H = 2.4 Hz, 2H, H₄/H₅), 6.12 (s, 2H, CH₂), 3.46 (s, 6H, CH₃).

NMR data are consistent with literature values.¹⁸

**1,1'-Ethylenebis(3-methylimidazole-2-thione) 84**

A solution of 43·2HCl (0.33 g, 1.3 mmol) in CH₃OH (5 mL) was added to a mixture of sulfur (0.08 g, 2.5 mmol) and K₂CO₃ (0.34 g, 2.5 mmol) in CH₃OH (10 mL). The mixture was stirred for overnight at room temperature. After that, the methanol was removed with a rotary evaporator. The residual powder was extracted by shaking with CH₂Cl₂ (30 mL) followed by filtration, and this process was repeated twice more. The CH₂Cl₂ extracts were combined and stripped of solvent (rotary evaporator) and the residue was recrystallised from CH₂Cl₂/CH₃OH to give the product as a white crystalline solid (0.25 g, 78.6%).

¹H NMR (600 MHz, DMSO-d₆): δ 7.08 (d, 3J_H,H = 2.4 Hz, 2H, H₄/H₅), 6.83 (d, 3J_H,H = 2.4 Hz, 2H, H₄/H₅), 4.30 (s, 4H, CH₂), 3.44 (s, 6H, CH₃).

NMR data are consistent with literature values.¹⁹
1,1’-(α-Xylylene)bis(3-methylimidazole-2-thione) 79

A solution of 1,1’-(α-xylylene)bis(3-methylimidazolium bromide) (0.5 g, 1.5 mmol) in CH₃OH (5 mL) was added to a mixture of sulfur (0.1 g, 3.5 mmol) and K₂CO₃ (0.5 g, 3.5 mmol) in CH₃OH (10 mL). The mixture was heated for overnight at 40 °C. After that, the methanol was removed with a rotary evaporator. The residual powder was extracted by shaking with CH₂Cl₂ (30 mL) followed by filtration, and this process was repeated twice more. The CH₂Cl₂ extracts were combined and stripped of solvent (rotary evaporator) and the residue was recrystallised from CH₂Cl₂/CH₃OH to give the product as a white crystalline solid (0.35 g, 67%).

¹H NMR (500 MHz, DMSO-d₆): δ 7.20 (d, 3J_H,H = 2.5 Hz, 2H, H₄/H₅), 7.02 (d, 3J_H,H = 2.5 Hz, 2H, H₄/H₅), 7.27-7.25 (m, 2H, H₄'/H₅'), 6.96-6.94 (m, 2H, H₃'/H₆'), 5.30 (s, 4H, 2 × benzylic CH₂), 3.51 (s, 6H, 2 × CH₃).

¹³C NMR (150.90 MHz, DMSO-d₆): 162.19 (C2), 134.49 (C₁'/C₂'), 127.80 (C₃'/C₆'), 127.72 (C₄'/C₅'), 119.02 (C₄'/C₅), 117.13 (C₄'/C₅), 47.38 (CH₂), 34.65 (CH₃).

Microanalysis: Found: C, 57.38; H, 5.34; N, 16.68; S, 18.94 % C₁₆H₁₈N₄S₂.(H₂O)₀.₂ requires C, 57.53; H, 5.55; N, 16.77; S, 19.19 %.

HRMS (APCI⁺): Calcd for C₁₆H₁₈N₄S₂ [M+H]⁺, m/z 331.1059. Found, m/z 331.1042.
1,1’-(o-Xylylene)bis(3-methylimidazole-2-thione) 80

A solution of 1,1’-(m-xylylene)bis(3-methylimidazolium bromide) (0.55 g, 1.6 mmol) in CH₃OH (5 mL) was added to a mixture of sulfur (0.1 g, 3.5 mmol) and K₂CO₃ (0.5 g, 3.5 mmol) in CH₃OH (10 mL). The mixture was heated for overnight at 40 °C. After that, the methanol was removed with a rotary evaporator. The residual powder was extracted by shaking with CH₂Cl₂ (30 mL) followed by filtration, and this process was repeated twice more. The CH₂Cl₂ extracts were combined and stripped of solvent (rotary evaporator) and the residue was recrystallised from CH₂Cl₂/CH₃OH to give the product as a white crystalline solid (0.15 g, 30%).

¹H NMR (500 MHz, DMSO-d₆): δ 7.30 (s, 1H, H2’), 7.29-7.27 (t, ³J_H,H = 4 Hz, 1H, H5’), 7.16 (d, ³J_H,H = 4 Hz, 2H, H4’/H6’), 7.14 (d, ³J_H,H = 2.5 Hz, 2H, H4/H5), 7.11 (d, ³J_H,H = 2.5 Hz, 2H, H4/H5), 5.17 (s, 4H, 2 × benzylic CH₂), 3.48 (s, 6H, 2 × CH3).

NMR data are consistent with literature values.²⁰
The *o*-cyclophane thione 31

A solution of *o*-cyclophane salt 30-2HBr (200 mg, 0.4 mmol) in CH$_3$OH (5 mL) was added to a mixture of sulfur (25 mg, 0.85 mmol) and K$_2$CO$_3$ (125 mg, 0.85 mmol) in CH$_3$OH (10 mL). The mixture was heated for overnight at 40 °C. The precipitate was collected by filtration and washed with small portions of H$_2$O and CH$_3$OH to give the product as a white powder (89 mg, 55 %).

$^1$H NMR (600 MHz, DMSO-$d_6$): δ 7.63-7.62 (m, 4H, H$4$/H$5'$), 7.51-7.49 (m, 4H, H$3$/H$6'$), 5.70 (s, 4H, H$4$/H$5$), 5.73-5.70 (d, $^2$J$_{H,H}$ = 14.5 Hz, 4H, benzylic HCH), 4.57-4.54 (d, $^2$J$_{H,H}$ = 14.5 Hz, 4H, benzylic HCH).

$^{13}$C NMR (125.75 MHz, DMSO-$d_6$): δ 161.34 (C$2$), 135.28 (C$1$/C$2'$), 133.52 (C$3$/C$6'$), 129.46 (C$4$/C$5'$), 116.13 (C$4$/C$5$), 48.94 (CH$_2$).

Microanalysis: Found: C, 65.39; H, 5.05; N, 13.51; S, 15.66 % C$_{22}$H$_{20}$N$_4$S$_2$ requires C, 65.32; H, 4.98; N, 13.85; S, 15.85 %.

HRMS (APCI$^+$): Calcd for C$_{22}$H$_{20}$N$_4$S$_2$ [M+H]$^+$, m/z 405.1208. Found, m/z 405.1202.

Crystals suitable for X-ray diffraction studies were grown by slow evaporation of a solution of the compound in 1:1 CH$_3$OH / CH$_2$Cl$_2$. 

A solution of \textit{m}-cyclophane salt \textit{32}\textperiodcentered2HBr (120 mg, 0.24 mmol) in CH\textsubscript{3}OH (5 mL) was added to a mixture of sulfur (16 mg, 0.48 mmol) and K\textsubscript{2}CO\textsubscript{3} (66 mg, 0.48 mmol) in CH\textsubscript{3}OH (10 mL). The mixture was heated for overnight at 40 °C. The precipitate was collected by filtration and washed with small portions of H\textsubscript{2}O and CH\textsubscript{3}OH to give the product as a white powder (70 mg, 72%).

\textsuperscript{1}H NMR (500 MHz, DMSO-\textit{d}_6): \(\delta\) 7.39 (m, 3H, H5'), 7.32-7.29 (m, 6H, H4'/H6'), 6.33 (s, 2H, \textit{anti} H2'), 6.23 (s, 1H, \textit{syn} H2'), 7.10 (s, 4H, \textit{anti} H4/H5), 6.93 (s, 2H, \textit{syn} H4/H5), 5.74 (d, \(\textit{J}_{H,H} = 16\) Hz, 2H, \textit{syn} benzyllic HCH), 5.62 (d, \(\textit{J}_{H,H} = 16\) Hz, 4H, \textit{anti} benzyllic HCH), 4.90 (d, \(\textit{J}_{H,H} = 16\) Hz, 4H, \textit{anti} benzyllic HCH), 4.86 (d, \(\textit{J}_{H,H} = 16\) Hz, 2H, \textit{syn} benzyllic HCH).

\textsuperscript{13}C NMR (125.75 MHz, DMSO-\textit{d}_6): \(\delta\) 163.38 (C2), 162.87 (C2), 137.78 (C1'/C3'), 137.63 (C1'/C3'), 128.40 (C5'), 128.29 (C5'), 126.02 (C4'/C6'), 125.80 (C4'/C6'), 121.98 (C2'), 121.94 (C2'), 118.08 (C4/C5), 117.71 (C4/C5), 49.47 (CH\textsubscript{2}), 49.31 (CH\textsubscript{2}).

Microanalysis: Found: C, 62.84; H, 4.88; N, 13.09; S, 15.04 % \textit{C}_{22}\textsubscript{H}_{20}\textsubscript{N}_{4}\textsubscript{S}_{2}.(H\textsubscript{2}O) requires C, 62.53; H, 5.25; N, 13.26; S, 15.17%. 

**The \textit{m}-cyclophane thione \textit{33}**
HRMS (APCI⁺): Calcd for C_{22}H_{20}N_{4}S_{2} [M+H]⁺, m/z 405.1208. Found, m/z 405.1174.

Crystals suitable for X-ray diffraction studies were grown by slow evaporation of a CH_{2}Cl_{2} solution of the compound.

The mesitylenophane thione 81

[Chemical structure image]

A solution of the mesitylenophane 77·2HBr (140 mg, 0.24 mmol) in CH_{3}OH (5 mL) was added to a mixture of sulfur (20 mg, 0.53 mmol) and K_{2}CO_{3} (70 mg, 0.5 mmol) in CH_{3}OH (10 mL). The mixture was heated for overnight at 40 °C. The precipitate was collected by filtration and washed with small portions of H_{2}O and CH_{3}OH to give the product as a white powder (40 mg, 35%).

^1H NMR (600 MHz, DMSO-d_{6}): δ 5.63 (s, 4H, H₄/H₅), 6.98 (s, 2H, H₅'), 5.54-5.51 (d, J_{H,H} = 14.4 Hz, 4H, benzylic HCH), 4.72-4.69 (d, J_{H,H} = 14.4 Hz, 4H, benzylic HCH), 2.39 (s, 12H, Hₐ), 1.56 (s, 6H, Hₚ).

^13C NMR (150.90 MHz, DMSO-d_{6}): δ 162.29 (C₂), 138.13 (C₂'), 136.66 (C₄'/C₆'), 133.51 (C₁'/C₃'), 129.77 (C₅'), 116.24 (C₄/C₅), 44.87 (C_{benzyllic}), 19.58 (Cₐ), 17.16 (Cₖ).

Microanalysis: Found: C, 68.59; H, 6.66; N, 11.60; S, 13.22 % C_{28}H_{32}N_{4}S_{2} requires C, 68.82; H, 6.60; N, 11.46; S, 13.12 %.
HRMS (APCI\(^+\)): Calcd for C\(_{28}\)H\(_{33}\)N\(_4\)S\(_2\) [M+H]\(^+\), \(m/z\) 489.2147. Found, \(m/z\) 489.2156.

Crystals suitable for X-ray diffraction studies were grown by slow evaporation of a solution of the compound in 1:1 CH\(_2\)Cl\(_2\) / ethyl acetate.

### 8.3.3 Au\(^{1+}\)-NHC complexes

**Bis(1,3-diisopropylimidazol-2-ylidene)gold(I) bromide 59·Br**

![Structural formula of Bis(1,3-diisopropylimidazol-2-ylidene)gold(I) bromide 59·Br](image)

K\(_2\)CO\(_3\) (0.7 g, 5 mmol) was added to a mixture of 1,3-diisopropylimidazolium bromide (0.1 g, 0.5 mmol) and Au(SMe\(_2\))Cl (0.07g, 0.25 mmol) in CH\(_3\)CN (25 mL). The mixture was stirred for 24 h at room temperature. After that, the resulting suspension was filtered and the solvent was removed under reduced pressure to give the product as a white solid. The white solid was recrystallised from a CH\(_3\)CN/Et\(_2\)O mixture to afford the desired complex as colourless crystals (0.2 g, 70%).

\(^1\)H NMR (500 MHz, DMSO-\(d_6\)): \(\delta\) 7.68 (s, 4H, H4/H5), 4.83 (sept., \(\text{J}_{\text{H,H}} = 13.5\) Hz, 4H, H1’), 1.49 (d, \(\text{J}_{\text{H,H}} = 6.5\) Hz, 24H, H2’).

Microanalysis: Found: C, 34.48, H, 5.63, N; 8.98. C\(_{18}\)H\(_{32}\)AuBrN\(_4\) 2.5(H\(_2\)O) requires C, 34.51, H, 5.95, N, 8.94%.

NMR data are consistent with literature values.\(^{21}\)
Bis(1,3-diisopropylimidazolin-2-ylidene)gold(I) hexafluorophosphate 59·PF$_6$

![Chemical structure of Bis(1,3-diisopropylimidazolin-2-ylidene)gold(I) hexafluorophosphate 59·PF$_6$]

A solution of KPF$_6$ (60 mg, 0.3 mmol) in water (3 mL) was added in a solution of 59·Br (50 mg, 0.08 mmol) in CH$_3$OH (5 mL). The precipitate was filtered off and washed with water (3 mL) and methanol ($3 \times 3$ mL).

$^1$H NMR (500 MHz, DMSO-$d_6$): $\delta$ 7.69 (s, 4H, H4/H5), 4.84 (sept., $^3$J$_{H,H}$ = 13.5 Hz, 4H, H1'), 1.50 (d, $^3$J$_{H,H}$ = 7 Hz, 24H, H2').

NMR data are consistent with literature values.$^{21}$

Microanalysis: Found: C, 28.92, H, 4.49, N; 7.28. C$_{18}$H$_{32}$AuF$_6$N$_4$P 5.5(H$_2$O) requires C, 29.00, H, 5.81, N, 7.52%.

The Au complex 62·2Cl

![Chemical structure of The Au complex 62·2Cl]

A solution of lithium butyrate (72 mg, 0.8 mmol) in DMF (10 mL) was added to a mixture of 42·2HCl (104 mg, 0.4 mmol) and Au(SMe$_2$)Cl (101 mg, 0.3 mmol) in DMF (10 mL) at 100 °C. The mixture was then heated to 120 °C and this temperature was
maintained overnight. During this time a white precipitate formed. The mixture was filtered while hot and the precipitate was washed once with each of DMF, acetone, Et₂O to leave 62·2Cl as a white solid (123 mg, 39%).

¹H NMR (600 MHz, DMSO-d₆): δ 7.92 (s, 4H, H4/H5), 7.60 (s, 4H, H4/H5), 7.20-7.18 (d, ²J_H,H = 14.4 Hz, 2H, HCH), 6.36-6.33 (d, ²J_H,H = 14.4 Hz, 2H, HCH), 3.88 (s, 12H, 4 × CH₃).


NMR data are consistent with literature values.²²

The Au complex 62·2PF₆

A solution of KPF₆ (750 mg, 0.4 mmol) in water (3 mL) was added in a solution of 62·2Cl (75 mg, 0.1 mmol) in methanol (10 mL). The white precipitate that formed was filtered off, washed with water (3 mL) and methanol (3 × 3 mL), and dried in vacuo to give 62·2PF₆ as a white powder (80 mg, 83%).

¹H NMR (500 MHz, DMSO-d₆): δ 7.91 (s, 4H, H4/H5), 7.61 (s, 4H, H4/H5), 7.20-7.17 (d, ²J_H,H = 13.5 Hz, 2H, HCH), 6.35-6.33 (d, ²J_H,H = 14.0 Hz, 2H, HCH), 3.89 (s, 12H, 4 × CH₃).
NMR data are consistent with literature values.\textsuperscript{22}

\textbf{The Au complex 56·2Cl}

\[
\begin{array}{c}
\text{N} \\
\text{Au} \\
\text{N} \\
\text{Au} \\
\text{N} \\
\text{N}
\end{array}
\]

A solution of lithium butyrate (69 mg, 0.75 mmol) in DMF (10 mL) was added to a mixture of 43·2HCl (108 mg, 0.4 mmol) and Au(SMe\textsubscript{2})Cl (98 mg, 0.3 mmol) in DMF (10 mL) at 100 °C. The mixture was then heated to 120 °C and this temperature was maintained for 5 h. During this time a white precipitate formed. The mixture was filtered while hot and the precipitate was washed once with each of DMF, acetone, and Et\textsubscript{2}O to give the product as a white solid (116 mg, 33 %).

\( ^{1}\text{H} \) NMR (600 MHz, DMSO-\textit{d}_6): \( \delta \) 7.44 (d, \( ^{3}\text{J}_{\text{H,H}} = 1.85 \text{ Hz}, 8\text{H}, \text{H}_4/\text{H}_5 \)), 7.41 (d, \( ^{3}\text{J}_{\text{H,H}} = 1.85 \text{ Hz}, 8\text{H}, \text{H}_4/\text{H}_5 \)), 4.79 (s, 8H, CH\textsubscript{2}CH\textsubscript{2}), 3.78 (s, 12H, 4 \times \text{CH}_3).

NMR data are consistent with literature values.\textsuperscript{23}
The Au complex 56·2PF₆

A solution of KPF₆ (700 mg, 0.38 mmol) in water (3 mL) was added in a solution of 56·2Cl (102 mg, 0.12 mmol) in methanol (10 mL). The white precipitate that formed was filtered off, washed with water (3 mL) and methanol (3 × 3 mL), and dried in vacuo to give 56·2PF₆ as a white powder (111 mg, 87%).

¹H NMR (600 MHz, DMSO- d₆): δ 7.44 (d, 3J_H,H = 1.86 Hz, 4H, H4/H5), 7.39 (d, 3J_H,H = 1.86 Hz, 4H, H4/H5), 4.78 (s, 8H, CH₂CH₂), 3.77 (s, 12H, 4 × CH₃).

NMR data are consistent with literature values.²³

The Au complex 65·2Cl

A solution of lithium butyrate (0.07 g, 0.75 mmol) in DMF (10 mL) was added to a mixture of 1,1'-(o-xylylene)bis(3-methylimidazolium chloride) (0.14 g, 0.4 mmol) and Au(SMe₂)Cl (0.1 g, 0.35 mmol) in DMF (10 mL) at 100 °C. The mixture was then heated to 120 °C and this temperature was maintained for 3 h. During this time a white
precipitate formed. The white precipitate was filtered off and washed once with each of DMF, acetone and Et₂O to give 65·2Cl as a white powder (0.2 g, 41%).

\(^1\)H NMR (600 MHz, DMSO-\(d_6\)): \(\delta 7.60\) (m, 8H, H3'/H6'), 7.57 (m, 8H, H4'/H5'), 7.20 (s, 4H, H4/H5), 6.68 (s, 4H, H4/H5), 5.67 (s, 8H, 4 \times \text{benzylic CH}_2), 3.75 (s, 12H, 4 \times \text{CH}_3).

NMR data are consistent with literature values.\(^\text{22}\)

**The Au complex 65·2Br\(^{22}\)**

A solution of lithium butyrate (0.07 g, 0.75 mmol) in DMF (10 mL) was added to a mixture of 1,1'-(o-xyylene)bis(3-methylimidazolium bromide) (0.18 g, 0.4 mmol) and Au(SMe\(_2\))Br (0.12 g, 0.35 mmol) in DMF (10 mL) at 100 °C. The mixture was then heated to 120 °C and this temperature was maintained for 4 h. During this time a white precipitate formed. The white precipitate was filtered off and washed once with each of DMF, acetone and Et₂O to give the product as a white powder (0.2 g, 46%).

\(^1\)H NMR (600 MHz, DMSO-\(d_6\)): \(\delta 7.59\) (m, 8H, H3'/H6'), 7.57 (m, 8H, H4'/H5'), 7.21 (s, 4H, H4/H5), 6.69 (s, 4H, H4/H5), 5.67 (s, 8H, 4 \times \text{benzylic CH}_2), 3.67 (s, 12H, 4 \times \text{CH}_3).

NMR data are consistent with literature values.\(^\text{22}\)
The Au complex 68·2Cl

A solution of lithium butyrate (0.07 g, 0.75 mmol) in DMF (10 mL) was added to a mixture of 1,1'-(m-xylylene)bis(3-methylimidazolium chloride) (0.14 g, 0.4 mmol) and Au(SMe₂)Cl (0.1 g, 0.35 mmol) in DMF (10 mL) at 100 °C. The mixture was then heated to 120 °C and this temperature was maintained for 5 h. During this time a white precipitate formed. The white precipitate was filtered off and washed once with each of DMF, acetone and Et₂O to give the desired product as a white powder (0.12 g, 30%).

¹H NMR (600 MHz, DMSO-d₆): δ 7.58 (d, 3J_H,H = 2.1 Hz, 4H, H4/H5), 7.52 (s, 3J_H,H = 2.1 Hz, 4H, H4/H5), 7.37 (t, 3J_H,H = 7.7 Hz, 2H, H5'), 7.25 (d, 3J_H,H = 7.7 Hz, 4H, H4'/H6'), 7.22 (s, 2H, H2'), 5.29 (s, 8H, 4 × benzylic CH₂), 3.45 (s, 12H, 4 × CH₃).

NMR data are consistent with literature values.²²
The Au complex 68·2Br

A solution of lithium butyrate (0.07 g, 0.75 mmol) in DMF (10 mL) was added to a mixture of 1,1'-(m-xylylene)bis(3-methylimidazolium bromide) (0.18 g, 0.4 mmol) and Au(SMe$_2$)Br (0.12 g, 0.35 mmol) in DMF (10 mL) at 100 °C. The mixture was then heated to 120 °C and this temperature was maintained for 6 h. During this time a white precipitate formed. The white precipitate was filtered off and washed once with each of DMF, acetone and Et$_2$O to give the required product as a white powder (0.25 g, 57%).

$^1$H NMR (600 MHz, DMSO-$d_6$): $\delta$ 7.37 (d, $^3$J$_{H,H}$ = 2 Hz, 4H, H4/H5), 7.39 (s, $^3$J$_{H,H}$ = 2 Hz, 4H, H4/H5), 7.35 (t, $^3$J$_{H,H}$ = 7.7 Hz, 2H, H5'), 7.23 (d, $^3$J$_{H,H}$ = 7.7 Hz, 4H, H4'/H6'), 7.21 (s, 2H, H2'), 5.29 (s, 8H, 4 × benzylic CH$_2$), 3.61 (s, 12H, 4 × CH$_3$).

NMR data are consistent with literature values.$^{22}$
The $o$-cyclophane-Au complex 11·2Cl

A solution of lithium acetate dihydrate (74 mg, 0.7 mmol) in DMF (10 mL) was added to a mixture of the $o$-cyclophane dichloride salt 30·2HCl (102 mg, 0.25 mmol) and Au(SMe$_2$)Cl (81 mg, 0.3 mmol) in DMF (10 mL) at 100 °C. The mixture was then heated to 120 °C and this temperature was maintained for 6 h. During this time a white precipitate formed. The white precipitate was filtered off and washed once with each of DMF, acetone and Et$_2$O. The crude white product was recrystallised from acetonitrile/ethyl acetate to give the desired compound as colourless crystals (96 mg, 36 %).

$^1$H NMR (500 MHz, DMSO-$d_6$): δ 7.81-7.80 (m, 8H, H3'/H6'), 7.63-7.61 (m, 8H, H4'/H5'), 6.40-6.37 (d, $^2$J$_{H,H} = 14.0$ Hz, 8H, HCH), 6.31 (s, 8H, H4/H5), 5.30-5.27 (d, $^2$J$_{H,H} = 14.5$ Hz, 8H, HCH).

NMR data are consistent with literature values.$^{22}$
The o-cyclophane-Au complex 11·2Br

A solution of lithium acetate dihydrate (75 mg, 0.7 mmol) in DMF (10 mL) was added to a mixture of the o-cyclophane dibromide salt 30·2HBr (131 mg, 0.25 mmol) and Au(SMe$_2$)Br (81 mg, 0.25 mmol) in DMF (10 mL) at 100 °C. The mixture was then heated to 120 °C and this temperature was maintained overnight. During this time a white precipitate formed. The white precipitate was filtered off and washed once with each of DMF, acetone and Et$_2$O. The crude white product was recrystallised from acetonitrile/ethyl acetate to give the target compound as colourless crystals (81 mg, 29%).

$^1$H NMR (600 MHz, DMSO-$d_6$): $\delta$ 7.81-7.80 (m, 8H, H3'/H6'), 7.62-7.61 (m, 8H, H4'/H5'), 6.39-6.37 (d, $^2$J$_{H,H}$ = 13.8 Hz, 8H, HCH), 6.31 (s, 8H, H4/H5), 5.30-5.27 (d, $^2$J$_{H,H}$ = 13.8 Hz, 8H, HCH).

NMR data are consistent with literature values.$^{22}$
The o-cyclophane-Au complex 11·2PF₆

A solution of KPF₆ (25 mg, 0.13 mmol) in water (3 mL) was added in a solution of the o-cyclophane-Au complex 11·2Cl (40 mg, 0.03 mmol) in methanol (10 mL). After that, the white precipitate was formed and filtered off. The white precipitate that formed was filtered off, washed with water (3 mL) and methanol (3 × 3 mL), and dried in vacuo to give 11·2PF₆ as a white powder (42 mg, 90 %).

¹H NMR (500 MHz, acetone-d₆): δ 7.75-7.74 (m, 8H, H3'/H6'), 7.64-7.62 (m, 8H, H4'/H5'), 6.46-6.43 (d, ²J_H,H = 14 Hz, 8H, HCH), 6.35 (s, 8H, H4/H5), 5.33-5.30 (d, ²J_H,H = 14 Hz, 8H, HCH).

NMR data are consistent with literature values.²²
The \textit{m}-cyclophane-Au complex 12·2Cl

A solution of lithium butyrate (70 mg, 0.75 mmol) in DMF (10 mL) was added to a mixture of the \textit{m}-cyclophane dichloride salt 32·2HCl (169 mg, 0.4 mmol) and Au(SMe$_2$)Cl (102 mg, 0.35 mmol) in DMF (10 mL) at 100 °C. The mixture was then heated to 120 °C and this temperature was maintained for 4 h. During this time a pink precipitate formed. The pink precipitate was filtered off and washed once with each of DMF, acetone and Et$_2$O. The crude white product was recrystallised from acetonitrile/ethyl acetate to give the desired compound as colourless crystals (260 mg, 59 %).

$^1$H NMR (600 MHz, DMSO-$d_6$): δ 7.35 (s, 8H, H4/H5), 7.20-7.18 (d, $^3$J$_{H,H}$ = 7.8 Hz, 8H, H4'/H6'), 7.08 (t, $^3$J$_{H,H}$ = 7.2 Hz, 4H, H5'), 5.70 (s, 4H, H2'), 5.33-5.30 (d, $^2$J$_{H,H}$ = 16.2 Hz, 8H, HCH), 5.20- 5.17 (d, $^2$J$_{H,H}$ = 16.2 Hz, 8H, HCH).

NMR data are consistent with literature values.$^{22}$
The \textit{m}-cyclophane-Au complex 12$\cdot$2Br$^{22}$

A solution of lithium acetate dihydrate (72 mg, 0.75 mmol) in DMF (10 mL) was added to a mixture of the \textit{m}-cyclophane dibromide salt 32$\cdot$2HBr (204 mg, 0.4 mmol) and Au(SMe$_2$)Br (115 mg, 0.35 mmol) in DMF (10 mL) at 100 °C. The mixture was then heated to 120 °C and this temperature was maintained for 4 h. During this time a white precipitate formed. The white precipitate was filtered off and washed once with each of DMF, acetone and Et$_2$O. The crude white product was recrystallised from acetonitrile/ethyl acetate to give the desired compound as colourless crystals (240 mg, 51%).

$^1$H NMR (600 MHz, DMSO-$d_6$): $\delta$ 7.35 (s, 8H, H4/H5), 7.20-7.18 (d, $^3$J$_{H,H} = 7.8$ Hz, 8H, H4'/H6'), 7.08 (t, $^3$J$_{H,H} = 7.2$ Hz, 4H, H5'), 5.70 (s, 4H, H2'), 5.33-5.31 (d, $^2$J$_{H,H} = 16.2$ Hz, 8H, HCH), 5.20- 5.17 (d, $^2$J$_{H,H} = 16.2$ Hz, 8H, HCH).

NMR data are consistent with literature values.$^{22}$
The Au complex $^{39}\cdot2Br$

A solution of LiOAc (0.027 g, 0.2646 mmol) in CH$_3$CN (5 mL) was added to a mixture of the ortho-cyclophane tetra-imidazolium salt $^{44}\cdot4HBr$ (0.04 g, 0.05 mmol) and Au(SMe$_2$)Cl (0.04 g, 0.1 mmol) in CH$_3$CN (15 mL). The mixture was refluxed overnight. During this time a white precipitate formed. The mixture was filtered while hot and the precipitate was washed with CH$_3$CN several times to give the product as a white powder (0.04 g, 86 %).

$^1$H NMR (600 MHz, DMSO-d$_6$): δ 8.04-8.02 (d, $^3$J$_{H,H}$ =12.6 Hz, 8H, H4/H5), 7.29-7.27 (m, 4H, H3'/H6'), 7.18-7.17 (m, 4H, H4'/H5'), 6.42-6.40 (d, $^2$J$_{H,H}$ =13.8 Hz, 2H, HCH), 6.34-6.32 (d, $^2$J$_{H,H}$ =13.8 Hz, 2H, HCH'), 5.77-5.74 (d, $^2$J$_{H,H}$ =14.7 Hz, 4H, benzylic HCH), 5.16-5.13 (d, $^2$J$_{H,H}$ =14.7 Hz, 4H, benzylic HCH').

NMR data are consistent with literature values.$^{12}$
The mesitylenophane Au complex 40·Br

A solution of lithium acetate dihydrate (73 mg, 0.7 mmol) in DMF (10 mL) was added to a mixture of the mesityleno-cyclophane salt 77·2HBr (220 mg, 0.4 mmol) and Au(SMe$_2$)Br (99 mg, 0.3 mmol) in DMF (15 mL) at 100 °C. The mixture was then heated to 120 °C and this temperature was maintained overnight. After that, the mixture was filtered while hot and the filtrate was concentrated in vacuo to 5 mL. The desired product was precipitated by addition of Et$_2$O (50 mL), collected by filtration, washed with Et$_2$O several times, and obtained as a white solid (92 mg, 35%).

$^1$H NMR (600 MHz, DMSO-$d_6$): δ 7.62 (s, 4H, H4/H5), 6.81 (s, 2H, H5'), 5.29-5.28 (d, $^2$J$_{H,H}$ = 6.6 Hz, 8H, benzylic CH$_2$), 2.30 (s, 6H, Hb), 1.84 (s, 12H, Ha).

NMR data are consistent with literature values.$^{24}$

Crystals suitable for X-ray diffraction studies were grown by diffusion of vapours between neat diethyl ether and a solution of the complex in acetonitrile.
8.3.4 \textit{Au}^{I}-IMT complexes

\textbf{Bis(1,3-dimethylimidazole-2-thione)gold(I) chloride 85·Cl}

A solution of 1,3-dimethylimidazole-2-thione 78 (38.5 mg, 0.3 mmol) in CHCl$_3$ (5 mL) was added to a solution of Au(SMe$_2$)Cl (44 mg, 0.15 mmol) in CHCl$_3$ (10 mL). The mixture was stirred 2 h at room temperature. After that, the white precipitate that formed and collected. The product was washed with diethyl ether several times to give the desired compound as a white solid (40 mg, 55%).

$^1$H NMR (600 MHz, DMSO-$d_6$): $\delta$ 7.39 (s, 4H, H4/H5), 3.66 (s, 12H, 4× CH$_3$).

$^{13}$C NMR (150.90 MHz, DMSO-$d_6$): $\delta$ 152.27 (C2), 120.67 (C4/C5), 35.39 (CH$_3$).

Microanalysis: Found: C, 20.80; H, 3.13; N, 9.47; S, 11.20 % AuC$_{10}$H$_{16}$N$_4$S$_2$Cl.(H$_2$O)$_{2.4}$ (CHCl$_3$)$_{0.55}$ requires C, 21.20; H, 3.60; N, 9.37; S, 10.73 %.

HRMS (APCI$^+$): Calcd for C$_{10}$H$_{16}$AuN$_4$S$_2$ [M-Cl]$^+$, m/z 453.0482. Found, m/z 453.0438.

Crystals suitable for X-ray diffraction studies were grown by slow evaporation of a dichloromethane solution of the complex.
Bis(1-ethyl-3-methylimidazole-2-thione)gold(I) chloride 86·Cl

A solution of 1-ethyl-3-methylimidazole-2-thione 82 (43 mg, 0.3 mmol) in CHCl₃ (5 mL) was added to a solution of Au(SMe₂)Cl (44 mg, 0.15 mmol) in CHCl₃ (10 mL). The mixture was stirred 2 h at room temperature. After that, the white precipitate was collected and washed with diethyl ether several times to give the desired product as a white solid (60 mg, 78%).

¹H NMR (600 MHz, DMSO-d₆): δ 7.38-7.42 (d, 3J_H,H = 17 Hz, 4H, H4/H5), 4.11(q, 3J_H,H = 7.5 Hz, 4H, H2'), 3.64 (s, 6H, H3'), 1.29 (t, 3J_H,H = 7.5 Hz, 6H, H1').

¹³C NMR (150.90 MHz, DMSO-d₆): δ 152.72 (C2), 121.28, 119.34 (C4/C5), 43.38 (C2'), 35.60 (C3'), 14.77 (C1').

HRMS (ESI⁺): Calcd for C₁₂H₂₀AuN₄S₂ [M-Cl]⁺, m/z 481.0795. Found, m/z 481.0796.

Microanalysis: Found: C, 26.95; H, 4.15; N, 10.48; S, 11.99 % AuC₁₂H₂₂N₄S₂Cl(H₂O) requires C, 26.52; H, 3.98; N, 10.08; S, 11.87 %.

Crystals suitable for X-ray diffraction studies were grown by slow evaporation of a dichloromethane solution of the complex.
The Au\textsuperscript{I} thione complex \textit{87·2Cl}

A solution of 1,1'-methylenebis(3-methylimidazole-2-thione) \textit{83} (24 mg, 0.1 mmol) in CH\textsubscript{2}Cl\textsubscript{2} (5 mL) was added to a solution of Au(SMe\textsubscript{2})Cl (30 mg, 0.1 mmol) in CH\textsubscript{2}Cl\textsubscript{2} (10 mL). The mixture was stirred for 5 h at room temperature. After that, the white precipitate was collected and washed with CH\textsubscript{2}Cl\textsubscript{2} several times to give the desired product as a white solid (49 mg, 52 \%).

\textsuperscript{1}H NMR (500 MHz, DMSO-\textit{d}\textsubscript{6}): \(\delta\) 7.48 (s, 4H, H4/H5), 7.30 (s, 4H, H4/H5), 6.24 (s, 4H, 2 \times CH\textsubscript{2}), 3.56 (s, 12H, 4 \times CH\textsubscript{3}).

\textsuperscript{13}C NMR (150.90 MHz, DMSO-\textit{d}\textsubscript{6}): 148.47 (C2), 123.82 (C4), 122.34 (C5), 59.38 (CH\textsubscript{2}), 36.36 (CH\textsubscript{3}).

Microanalysis: Found: C, 22.67; H, 2.98; N, 11.77; S, 13.84 \% Au\textsubscript{2}C\textsubscript{18}H\textsubscript{24}N\textsubscript{8}S\textsubscript{4}Cl\textsubscript{2} requires C, 22.87; H, 2.56; N, 11.85; S, 13.56 \%.

HRMS (ESI\textsuperscript{+}): Calcd for Au\textsubscript{2}C\textsubscript{18}H\textsubscript{24}N\textsubscript{8}S\textsubscript{4}Cl\textsubscript{2} \textsuperscript{+} [M-Cl]\textsuperscript{+}, \(m/z\) 909.0027. Found, \(m/z\) 909.0073

Crystals suitable for X-ray diffraction studies were grown by slow evaporation of an acetone solution of the complex.
The Au(I) thione complex 88·2Cl

A solution of 1,1’-ethylenebis(3-methylimidazole-2-thione) 84 (25 mg, 0.098 mmol) in CH₂Cl₂ (5 mL) was added to a solution of Au(SMe₂)Cl (29 mg, 0.098 mmol) in CH₂Cl₂ (10 mL). The mixture was stirred overnight at room temperature. After that, the white precipitate was collected and washed several times with CH₂Cl₂ to give the desired compound as a white solid (40 mg, 42 %).

¹H NMR (600 MHz, DMSO-d₆): δ 7.38 (s, 4H, H4/H5), 7.24 (s, 4H, H4/H5), 4.57 (s, 8H, H1’), 3.64 (s, 12H, 4 × CH₃).

¹³C NMR (150.90 MHz, DMSO-d₆): δ 153.83 (C2), 121.18 (C5), 119.59 (C4), 46.72 (C1’), 35.39 (CH₃).

Microanalysis: Found: C, 24.55; H, 2.84; N, 11.29; S, 12.98 % Au₂C₂₀H₂₈N₈S₄Cl₂ requires C, 24.67; H 2.90; N, 11.51; S, 13.17 %.

HRMS (ESI⁺): Calcd for Au₂C₂₀H₂₈N₈S₄Cl⁺ [M-Cl]⁺, m/z 937.0340. Found, m/z 937.0396.

Crystals suitable for X-ray diffraction studies were grown by diffusion of vapours between neat diethyl ether and a solution of the complex in methanol.
The Au\textsuperscript{1} thione complex \textit{89}\cdot PF\textsubscript{6}

A solution of 1,1'-(\textit{o}-xylylene)bis(3-methylimidazole-2-thione) \textit{79} (27 mg, 0.08 mmol) in CH\textsubscript{2}Cl\textsubscript{2} (5 mL) was added to a solution of Au(SMe\textsubscript{2})Cl (23.5 mg, 0.08 mmol) in CH\textsubscript{2}Cl\textsubscript{2} (10 mL). The mixture was stirred for 6 h at room temperature. After that, the white precipitate was collected and washed several times with CH\textsubscript{2}Cl\textsubscript{2} to give the Au-thione complex \textit{89}\cdot 2Cl as a white solid (50 mg, 56 \%). The white solid was dissolved in methanol (5 mL) and a solution of KPF\textsubscript{6} (17 mg, 0.1 mmol) in water (5 mL) was added. The precipitate was filtered off and washed with water (5 mL) and methanol (3 \times 3 mL) to leave the desired product \textit{89}\cdot PF\textsubscript{6} as colourless crystals. X-ray studies showed that the product was dimeric (\textit{89d}\cdot 2PF\textsubscript{6}) in the solid state, while NMR and mass spectrometry studies suggested that the product existed in solution as a mixture of monomeric (\textit{89m}\cdot PF\textsubscript{6}) and dimeric (\textit{89d}\cdot 2PF\textsubscript{6}) species.

\textsuperscript{1}H NMR (500 MHz, DMSO-\textit{d}\textsubscript{6}): \textit{δ} 7.50-7.49 (d, \textit{J}_{\text{H,H}} = 2 \text{ Hz}, 4\text{H}, H4/H5), 7.35 (d, \textit{J}_{\text{H,H}} = 2 \text{ Hz}, 4\text{H}, H4/H5), 7.33-7.31 (m, 4\text{H}, H3'/H6'), 6.97-6.95 (m, 4\text{H}, H4'/H5'), 5.52 (s, 8\text{H}, 4 \times \text{benzylic CH}_2), 3.69 (s, 12\text{H}, 4 \times \text{CH}_3).
$^{13}$C NMR (125.75 MHz, DMSO-$d_6$): δ154.04 (C2), 133.35 (C1'/C2'), 128.27 (C3'/C6'), 127.84 (C4'/C5'), 121.28 (C4/C5), 119.82 (C4/C5), 48.31 (CH$_2$), 35.46 (CH$_3$).

Microanalysis: Found: C, 28.63; H, 2.69; N, 8.42; S, 9.85 % Au$_2$C$_{32}$H$_{36}$N$_8$S$_4$P$_2$F$_{12}$ requires C, 28.58; H 2.70; N, 8.33; S, 9.54 %.

HRMS (ESI$^+$): Calcd for (89d·2PF$_6$) Au$_2$C$_{32}$H$_{36}$N$_8$S$_4$PF$_6$ $^+$ [M-PF$_6$]$^+$, $m/z$ 1199.0919. Found, $m/z$ 1199.0927. Calcd for (89m·PF$_6$) AuC$_{16}$H$_{18}$N$_4$S$_2$ $^+$ [M-PF$_6$]$^+$, $m/z$ 527.0639. Found, $m/z$ 527.0626.

Crystals suitable for X-ray diffraction studies were grown by slow evaporation of an acetone solution of the complex.

The Au$^+$ thione complex 90·PF$_6$

A solution of 1,1'-(m-xylene)bis(3-methylimidazole-2-thione) 80 (27 mg, 0.08 mmol) in CH$_2$Cl$_2$ (5 mL) was added to a solution of Au(SMe)$_2$Cl (23.5 mg, 0.08 mmol) in CH$_2$Cl$_2$ (10 mL). The mixture was stirred overnight at room temperature. After that, the white precipitate was collected and washed several times with CH$_2$Cl$_2$ to give the Au-
thione complex 90·Cl as white solid (41 mg, 91 %). The white solid was dissolved in methanol (5 mL) and a solution of KPF₆ (13 mg, 0.08 mmol) in water (5 mL) was added. The precipitate was filtered off and washed with water (5 mL) and methanol (3× 3 mL) to leave the desired product 90·PF₆ as colourless crystals. X-ray studies showed that the product was monomeric (90m·PF₆) in the solid state, while NMR and mass spectrometry studies suggested that the product existed in solution as a mixture of monomeric (90m·PF₆) and dimeric (90d·2PF₆) species.

¹H NMR (600 MHz, DMSO-d₆): δ 7.54 (d, 3J_H,H = 2 Hz, 2H, H4/H5), 7.49 (d, 3J_H,H = 2 Hz, 2H, H4/H5), 7.39-7.37 (t, 3J_H,H = 8 Hz, 1H, H5'), 7.32 (d, 3J_H,H = 2 Hz, 2H, H4'/H6'), 7.30 (s, 1H, H2'), 5.35 (s, 4H, benzylic CH₂), 3.69 (s, 6H, CH₃).

¹³C NMR (150.90 MHz, DMSO-d₆): δ 152.06 (C2), 135.87 (C1'/C3'), 129.21 (C5'), 127.19 (C4'/C6'), 126.92 (C2'), 121.59 (C4/C5), 120.18 (C4/C5), 50.61 (CH₂), 35.52 (CH₃).

Microanalysis: Found: C, 28.98; H, 2.57; N, 8.19; S, 9.58 % AuC₁₆H₁₈N₄S₂PF₆ requires C, 28.58; H 2.70; N, 8.33; S, 9.54 %.


Crystals suitable for X-ray diffraction studies were grown by slow evaporation of an acetone solution of the complex.
The Au\(^1\) m-cyclophane thione complexes 91 and 92·Cl

A solution of the \(m\)-cyclophane thione \(33\) (16 mg, 0.04 mmol) in CH\(_2\)Cl\(_2\) (5 mL) was added to a solution of Au(SMe\(_2\))Cl (13 mg, 0.044 mmol) in CH\(_2\)Cl\(_2\) (5 mL). The mixture was stirred overnight at room temperature. After that, the white precipitate was collected and washed several times with CH\(_2\)Cl\(_2\) to give a white solid (15 mg) which was shown by \(^1\)H NMR spectroscopy to contain 91 and 92·Cl in a ratio of 2:1 (yields: 91, 28%; 92·Cl, 14%).

\(^1\)H NMR (600 MHz, DMSO-\(d_6\), 80 °C) for (91): \(\delta\) 7.43 (t, \(^3\)\(J_{H,H} = 7.5\) Hz, 2H, H5'), 7.33 (d, \(^3\)\(J_{H,H} = 7.5\) Hz, 4H, H4'/H6'), 7.15 (s, 4H, H4/H5), 6.35 (s, 2H, H2'), 5.71 (d, \(^2\)\(J_{H,H} = 16.2\) Hz, 4H, 4 × benzylic \(HCH\)), 4.97 (br s, 4H, 4 × benzylic \(HCH\)).

\(^{13}\)C NMR (150.90 MHz, DMSO-\(d_6\)) for (91): \(\delta\) 136.64 (C1'/ C3'), 128.97 (C5'), 126.73 (C4'/ C6'), 121.28 (C2'), 121.51 (C4/C5), 50.46 (benzylic CH\(_2\)), not seen (C2).

\(^1\)H NMR (600 MHz, DMSO-\(d_6\), 80 °C) for (92·Cl): \(\delta\) 7.52 (t, \(^3\)\(J_{H,H} = 7.5\) Hz, 2H, H5'), 7.40 (d, \(^3\)\(J_{H,H} = 7.5\) Hz, 4H, H4'/H6'), 7.61 (s, 4H, H4/H5), 6.29 (s, 2H, H2'), 5.63 (d, \(^2\)\(J_{H,H} = 16.3\) Hz, 4H, 4 × benzylic \(HCH\)), 5.43 (d, \(^2\)\(J_{H,H} = 16.3\) Hz, 4H, 4 × benzylic \(HCH\)).
$^{13}$C NMR (150.90 MHz, DMSO-$d_6$) for (92·Cl): $\delta$ 148.97 (C2), 134.71 (C1' / C3'), 129.36 (C5'), 126.54 (C4' / C6'), 120.79 (C2'), 123.06 (C4/C5), 51.23 (benzylic CH$_2$).

Microanalysis: Found: C, 33.35; H, 2.53; N, 6.75; S, 7.91 %. Mixture of (91) and (92·Cl) [2:1, (Au$_2$C$_{22}$H$_{20}$N$_4$S$_2$Cl)$_2$(AuC$_{22}$H$_{20}$N$_4$S$_2$Cl)] requires C, 33.37; H 2.55; N, 7.07; S, 8.10 %.

HRMS (ESI$^+$): Calcd for (92·Cl) AuC$_{22}$H$_{20}$N$_4$S$_2$ $^+$ [M-Cl]$^+$, $m/z$ 601.0795. Found, $m/z$ 601.0762.

Diffusion of vapours between acetone and a solution of the product mixture in DMSO gave crystals of 91 suitable for X-ray diffraction studies.

The mesitylenophane thione Au$^+$ complex 93·Cl

A solution of the mesitylenophane thione 81 (20 mg, 0.04 mmol) in CH$_2$Cl$_2$ (5 mL) was added to a solution of Au(SMe$_2$)Cl (12 mg, 0.04 mmol) in CH$_2$Cl$_2$ (5 mL). The mixture was stirred overnight at room temperature. After that, the white precipitate was collected and was washed several times with CH$_2$Cl$_2$ to give 93·Cl as a white solid (15 mg, 53 %).
\(^1\)H NMR (500 MHz, DMSO-\(d_6\)): \(\delta 7.87\) (s, 4H, H4/H5), 6.83 (s, 2H, H5''), 5.38-5.35 (d, \(^2\)J\(_{HH}\) = 15.8 Hz, 4H, 4 \times benzyllic HCH), 5.24-5.21 (d, \(^2\)J\(_{HH}\) = 15.8 Hz, 4H, 4 \times benzyllic HCH), 2.43 (s, 12H, Ha), 1.50 (s, 6H, Hb).

\(^{13}\)C NMR (125.75 MHz, DMSO-\(d_6\)): \(\delta 146.78\) (C2), 138.60 (C2''), 135.81 (C4'/ C6''), 129.95 (C1'/ C3''), 129.46 (C5''), 123.85 (C4'/ C5), 48.74 (benzyllic CH\(_2\)), 20.53 (Ca), 18.20 (Cb).

Microanalysis: Found: C, 46.83; H, 4.27; N, 7.90; S, 8.94 % AuC\(_{28}\)H\(_{32}\)N\(_4\)S\(_2\)Cl requires C, 46.64; H 4.47; N, 7.77; S, 8.89 %.

HRMS (ESI\(^+\)): Calcd for AuC\(_{28}\)H\(_{32}\)N\(_4\)S\(_2\)\(^+\) [M-Cl]\(^+\), \(m/z\) 685.1734. Found, \(m/z\) 685.1766.

Crystals suitable for X-ray diffraction studies were grown by slow evaporation of a methanol solution of the complex.

**The o-cyclophane thione Au\(^1\) complex 94·Cl**

A solution of the o-cyclophane thione 33 (16 mg, 0.04 mmol) in CH\(_2\)Cl\(_2\) (5 mL) was added to a solution of Au(SMe\(_2\))Cl (13 mg, 0.044 mmol) in CH\(_2\)Cl\(_2\) (5 mL). The mixture immediately became dark blue, suggesting that gold colloids were formed. The
mixture was stirred for 2 h at 0 °C. After that, the pale blue solid was collected and washed several times with CH$_2$Cl$_2$ to give the crude product, tentatively assigned as 94·Cl, as a pale blue solid (35 mg). Numerous attempts to grow single crystals for X-ray studies were unsuccessful, affording only crystals of the o-cyclophane thione 33.

$^1$H NMR (600 MHz, DMSO-$d_6$): $\delta$ 7.67 (br s, 8H, H4'/H5'), 7.55-7.53 (m, 8H, H3'/H6'), 5.80 (s, 4H, H4/H5), 5.78 (s, 4H, H4/H5), (br s, 8H, benzylic HCH), 4.72 (br s, 8H, benzylic HCH).

HRMS (ESI$^+$): Calcd for AuC$_{44}$H$_{40}$N$_8$S$_4^+$ [M-Cl]$^+$, m/z 1005.1924. Found, m/z 1005.1298.
8.3.5 \textit{Au}^{III}-NHC complexes

**Dibromobis(1,3-diisopropylimidazolin-2-ylidene)gold(III) bromide 60·Br**

![Chemical structure of Dibromobis(1,3-diisopropylimidazolin-2-ylidene)gold(III) bromide 60·Br]

A solution of bromine (1.5 \( \mu \text{L}, 0.03 \text{ mmol}) in CH\(_3\)CN (5 mL) was added to a solution of 59·Br (12 mg, 0.02 mmol) in CH\(_3\)CN (5 mL) at -45°C. The mixture was stirred 2 h at the same temperature. After that, the mixture was heated to room temperature and evaporated under reduced pressure to give yellow solid, which was washed with Et\(_2\)O several times and dried \textit{in vacuo} to leave 60·Br as yellow solid (12 mg, 86%).

\(^1\)H NMR (500 MHz, DMSO-d\(_6\)): \( \delta \) 8.04 (s, 4H, H4/H5), 4.72 (sept., \(^3\)J\(_{H,H} = 13.0\) Hz, 4H, H1'), 1.54-1.52 (d, \(^3\)J\(_{H,H} = 6.5\) Hz, 24H, H2').

\(^{13}\)C NMR (125.75 MHz, DMSO-d\(_6\)): \( \delta \) 147.07(C2), 121.97 (C4/C5), 53.81 (C1'), 22.72 (C2').

Microanalysis: Found C, 28.92; H, 4.49; N, 7.28\%; AuC\(_{18}\)H\(_{32}\)N\(_4\)Br\(_3\) requires C, 29.17; H, 4.35; N, 7.56\%.

Crystals suitable for X-ray diffraction studies were grown by diffusion of vapours between neat diethyl ether and a solution of the complex in acetonitrile.
Dibromobis(1,3-diisopropylimidazolin-2-ylidene)gold(III) hexafluorophosphate
60·PF₆

A solution of bromine (1.5 µL, 0.03 mmol) in CH₃CN (5 mL) was added to a solution of
59·PF₆ (13 mg, 0.02 mmol) in CH₃CN (5 mL) at -45 °C. The mixture was stirred 2 h at
the same temperature for 2 h. After that, the mixture was heated to room temperature
and evaporated under reduced pressure to give yellow solid, which was washed with
Et₂O several times and dried *in vacuo* afford 60·PF₆ as yellow solid (15 mg, 93%).

¹H NMR (600 MHz, DMSO-d₆): δ 8.04 (s, 4H, H4/H5), 4.72 (sept., ³J_H,H = 13.2 Hz, 4H,
H1’), 1.54-1.52 (d, ³J_H,H = 6.6 Hz, 24H, H2’).

³¹P NMR (242.93 MHz, DMSO-d₆): δ -144.21 (sept., ¹J_P,F = 710.8 Hz, PF₆).

Crystals suitable for X-ray diffraction studies were grown by slow evaporation of an
acetone solution of the complex.
The dinuclear Au\textsuperscript{III} complex 57·2Br

A solution of bromine (3 µL, 0.06 mmol) in CH\textsubscript{3}CN (5 mL) was added to a solution of 62·2PF\textsubscript{6} (21 mg, 0.02 mmol) in CH\textsubscript{3}CN (5 mL). The mixture was stirred overnight at room temperature. After that, the mixture was evaporated under reduced pressure to leave a yellow solid which was washed with Et\textsubscript{2}O several times and dried \textit{in vacuo} to give 57·2Br as yellow solid (20 mg, 66%).

\textsuperscript{1}H NMR (500 MHz, DMSO-\textit{d}\textsubscript{6}): \( \delta \) 8.36 (s, 4H, H4/H5), 8.02 (s, 4H, H4/H5), 6.98-6.97 (d, \( ^2J_{\text{H,H}} = 5.5 \) Hz, 4H, 2 × CH\textsubscript{2}), 4.06 (s, 12H, 4 × CH\textsubscript{3}).

Crystals suitable for X-ray diffraction studies were grown by diffusion of vapours between neat diethyl ether and a solution of the complex in acetonitrile.

NMR data are consistent with literature values.\textsuperscript{25}
The dinuclear Au$^{III}$ complex 55·2Cl

![Diagram of 55·2Cl]

Thionyl chloride (30.5 μL, 0.4 mmol) was added to a solution of 62·2Cl (19 mg, 0.03 mmol) in CH$_3$CN (10 mL). The mixture was stirred overnight at room temperature. After that, the mixture was evaporated under reduced pressure to give white solid. The solid was washed with Et$_2$O several times and dried in vacuo to leave 55·2Cl as a white solid (9 mg, 38%).

$^1$H NMR (500 MHz, DMSO-$d_6$): δ 8.45 (s, 4H, H4/H5), 7.97 (s, 4H, H4/H5), 7.13-7.11 (d, $^2$J$_{H,H}$ = 14.5 Hz, 2H, 2 × CH$_2$), 6.99-6.97 (d, $^2$J$_{H,H}$ = 14.5 Hz, 2H, 2 × CH$_2$), 4.11 (s, 12H, 4 × CH$_3$).

NMR data are consistent with literature values.$^{26}$

The dinuclear Au$^{III}$ complex 58·2Br

![Diagram of 58·2Br]

A solution of bromine (7 μL, 0.1 mmol) in CH$_3$CN (5 mL) was added to a solution of 56·2PF$_6$ (32 mg, 0.03 mmol) in CH$_3$CN (5 mL). The mixture was stirred overnight at
room temperature. After that, the mixture was evaporated under reduced pressure to give yellow solid. The solid was washed with Et₂O several times and dried *in vacuo* to leave 58·2Br as yellow solid (38 mg, 89%).

\[ ^1H \text{ NMR (600 MHz, DMSO-}d_6\text{): } \delta 8.12 \text{ (s, 4H, H4/H5), 7.89 (s, 4H, H4/H5), 4.72 (s, 8H, CH}_2\text{CH}_2, 4.00 (s, 12H, 4} \times \text{ CH}_3). \]

NMR data are consistent with literature values.²⁵

The dinuclear Au\textsuperscript{III} complex 74·2Cl

Thionyl chloride (24 µL, 0.3 mmol) was added to a solution of 65·2Cl (23 mg, 0.03 mmol) in CH₃CN (10 mL). The mixture was stirred overnight at room temperature. After that, the mixture was evaporated under reduced pressure to give brown solid. The solid was washed with Et₂O several times and dried *in vacuo* to leave 74·2Cl as a brown solid (16 mg, 54%).

\[ ^1H \text{ NMR (600 MHz, DMSO-}d_6\text{): } \delta 7.87-7.87 \text{ (d, } ^3J_{H,H} = 1.8 \text{ Hz, 4H, H4/H5), 7.57-7.56 (d, } ^3J_{H,H} = 1.8 \text{ Hz, 4H, H4/H5), 7.15 (br s, 4H, H3'/ H6'), 6.45 (br s, 4H, H4'/ H5''), 5.73 (m, 8H, 4} \times \text{ benzylic CH}_2, 4.11 \text{ (s, 12H, 4} \times \text{CH}_3). \]
Crystals suitable for X-ray diffraction studies were grown by diffusion of vapours between neat diethyl ether and a solution of the complex in methanol.

NMR data are consistent with literature values.\textsuperscript{27}

The dinuclear Au\textsuperscript{III} complex 66·2Br

A solution of bromine (6 µL, 0.1 mmol) in CH\textsubscript{3}CN (5 mL) was added to a solution of 65·2Br (41 mg, 0.04 mmol) in CH\textsubscript{3}CN (5 mL). The mixture was stirred overnight at room temperature. After that, the mixture was evaporated under reduced pressure to give yellow solid. The solid was washed with Et\textsubscript{2}O several times and dried \textit{in vacuo} to give 66·2Br as a yellow solid (55 mg, 97%).

\textsuperscript{1}H NMR (500 MHz, DMSO-\textit{d}\textsubscript{6}): \(\delta\) 7.89-7.88 (d, \(^3\)J\textsubscript{H,H} = 2 Hz, 4H, H4/H5), 7.56-7.56 (d, \(^3\)J\textsubscript{H,H} = 2 Hz, 4H, H4/H5), 7.19 (br s, 4H, H3'/H6'), 6.53 (br s, 4H, H4'/H5'), 5.69 (m, 8H, 4 \times\text{benzylic CH}_2), 4.04 (s, 12H, 4 \times\text{CH}_3).

\textsuperscript{13}C NMR (125.75 MHz, DMSO-\textit{d}\textsubscript{6}): 150.22 (C2), 8132.18 (C1'/C2'), 128.08 (C3'/C6'), 126.12 (C4'/C5'), 126.89 (C4/C5), 124.66 (C4/C5), 50.07 (CH\textsubscript{2}), 37.60 (CH\textsubscript{3}).

NMR data are consistent with literature values.\textsuperscript{27}
The dinuclear $\text{Au}^{III}$ complex $69\cdot2\text{Br}$

A solution of bromine (7 $\mu$L, 0.1 mmol) in CH$_3$CN (5 mL) was added to a solution of $68\cdot2\text{Br}$ (30 mg, 0.03 mmol) in CH$_3$CN (5 mL). The mixture was stirred overnight at room temperature. After that, the mixture was evaporated under reduced pressure to give yellow solid, which was washed with Et$_2$O several times and dried in vacuo to afford $69\cdot2\text{Br}$ as a yellow solid (35 mg, 87%).

$^1$H NMR (500 MHz, DMSO-$d_6$): $\delta$ 7.78-7.77 (d, $^3J_{\text{H,H}} = 2$ Hz, 4H, H4/H5), 7.61-7.60 (s, $^3J_{\text{H,H}} = 2$ Hz, 4H, H4/H5), 7.42 (s, 2H, H2'), 7.40-7.37 (t, $^3J_{\text{H,H}} = 7.7$ Hz, 2H, H5'), 7.01-6.99 (d, $^3J_{\text{H,H}} = 7.7$ Hz, 4H, H4'/H6'), 5.08 (s, 8H, 4 × benzylic CH$_2$), 3.96 (s, 12H, 4 × CH$_3$).

NMR data are consistent with literature values.$^{27}$
The dinuclear Au$^{III}$ complex 75·2Cl

Thionyl chloride (27 µL, 0.4 mmol) was added to a solution of 68·2Cl (26 mg, 0.03 mmol) in CH$_3$CN (10 mL). The mixture was stirred overnight at room temperature. After that, the mixture was evaporated under reduced pressure to give brown solid. The solid was washed with Et$_2$O several times and dried in vacuo and 75·2Cl was obtained as a yellow solid (24 mg, 84%).

$^1$H NMR (500 MHz, DMSO-$d_6$): δ 7.76 (d, $^3$J$_{H,H} = 1.3$ Hz, 4H, H4/H5), 7.61 (s, $^3$J$_{H,H} = 1.3$ Hz, 4H, H4/H5), 7.40-7.37 (t, $^3$J$_{H,H} = 7.5$ Hz, 2H, H5$'$), 7.36 (s, 2H, H2$'$), 6.93-6.92 (d, $^3$J$_{H,H} = 7.5$ Hz, 4H, H4$'$/H6$'$), 5.08 (s, 8H, 4 × benzylic CH$_2$), 4.02 (s, 12H, 4 × CH$_3$).

Crystals suitable for X-ray diffraction studies were grown by diffusion of vapours between neat diethyl ether and a solution of the complex in methanol.

NMR data are consistent with literature values.$^{27}$
Tricyanido(1,3-diisopropylimidazolin-2-ylidene)gold(III) 61

A solution of NaCN (13 mg, 0.25 mmol) in water (5 mL) was added to a solution of 
60·Br (45 mg, 0.06 mmol) in methanol (10 mL). The mixture was stirred for 2 h at 
room temperature. After that, the white precipitate that had formed was collected, 
washed with water several times and dried *in vacuo* to leave 61 as a white solid (15 mg, 
56%).

$^1$H NMR (500 MHz, DMSO-$d_6$): $\delta$ 8.12 (s, 4H, H4/H5), 4.92 (sept., $^3$J$_{H,H}$ = 13.0 Hz, 4H, 
H1'), 1.42-1.41 (d, $^3$J$_{H,H}$ = 6.5 Hz, 24H, H2').

$^{13}$C NMR (125.75 MHz, DMSO-$d_6$): $\delta$ 132.35(C2), 122.17 (C4/C5), 110.54 (CN), 53.11 
(C1'), 22.32 (C2').

Microanalysis: Found: C, 34.09; H, 3.80; N, 16.75 % AuC$_{12}$H$_{16}$N$_5$ requires C, 33.73; H, 
3.77; N, 16.39 %.

HRMS (ESI$^+$): HRMS (ESI$^+$): Calcd for AuC$_{12}$H$_{17}$N$_5$\(^+\) ([M+H]$^+$), m/z 428.1150. Found, 
m/z 428.1124.

Crystals suitable for X-ray diffraction studies were grown by slow evaporation of an 
acetonitrile solution of the complex.
The dicyanido Au^{III} complex 63·Br

A solution of NaCN (23 mg, 0.47 mmol) in water (5 mL) was added to a solution of 57·2Br (135 mg, 0.12 mmol) in methanol (15 mL). The mixture was stirred for 3 h at room temperature. The white precipitate that formed was collected, washed with water several times and recrystallized from CH₂Cl₂ to give 63·Br as colourless crystals (56 mg, 46%).

¹H NMR (500 MHz, DMSO-d₆): δ 7.87 (d, ³J_H,H = 2 Hz, 2H, H₄/H₅), 7.77 (d, ³J_H,H = 2 Hz, 2H, H₄/H₅), 6.57-6.55 (d, ²J_H,H = 10 Hz, 2H, CH₂), 4.06 (s, 6H, 2 × CH₃).

¹³C NMR (125.75MHz, DMSO-d₆): δ 140.86 (C2), 125.12 (C4), 123.52 (C5), 109.55 (C₃'), 62.58 (CH₂), 39.15 (CH₃).

Microanalysis: Found: C, 25.38; H, 2.22; N, 14.97 % AuC₁₁H₁₂N₆Br(CH₂Cl₂)₀.₅ requires C, 25.22; H, 2.39; N, 15.35 %.


Crystals suitable for X-ray diffraction studies were grown by slow evaporation of an acetonitrile solution of the complex.
The dicyanido Au[III] complex 64·AuBr₄

A solution of NaCN (12 mg, 0.23 mmol) in water (5 mL) was added to a solution of 58·2Br (73 mg, 0.058 mmol) in methanol (10 mL). The mixture was stirred for 3 h at room temperature. After that, the white precipitate was collected, washed with water several times and recrystallized from CH₂Cl₂ to give 64·AuBr₄ as colourless crystals (45 mg, 52%).

¹H NMR (600 MHz, DMSO-ｄ₆): δ 7.78 (d, 3J_H,H = 2 Hz, 2H, H₄/H₅), 7.76 (d, 3J_H,H = 2 Hz, 2H, H₄/H₅), 5.12- 5.06 (m, 2H, CH₂CH₂), 4.70- 4.65 (m, 2H, CH₂CH₂), 3.96 (s, 6H, 2 × CH₃).

¹³C NMR (150.9 MHz, DMSO-ｄ₆): δ 137.08 (C2), 126.03 (C5), 125.35 (C4), 112.46 (C3’), 47.18 (CH₂CH₂), 38.84 (CH₃).

Microanalysis: Found: C, 14.63; H, 1.57; N, 7.82 % Au₂C₁₂H₁₄N₆Br₄(CH₂Cl₂) requires C, 15.00; H, 1.55; N, 8.08 %.


Crystals suitable for X-ray diffraction studies were grown by slow evaporation of an acetonitrile solution of the complex.
The dicyanido Au$^{III}$ complex 67·Au(CN)$_4$

A solution of NaCN (10 mg, 0.2 mmol) in water (5 mL) was added to a solution of 66·2Br (70 mg, 0.05 mmol) in methanol (15 mL). The mixture was stirred for 3 h at room temperature. After that, the white precipitate was collected, washed with water several times and recrystallized from CH$_2$Cl$_2$ to give syn-67·Au(CN)$_4$ as colourless crystals (38 mg, 50%).

$^1$H NMR (500 MHz, CD$_3$CN) for (syn-67$^+$): $\delta$ 7.71-7.69 (m, 2H, H3'/H6'), 7.63-7.61 (m, 4H, H4'/H5'), 7.57-7.56 (d, $^3$J$_{H,H}$ = 2 Hz, 2H, H4/H5), 7.40 (d, $^3$J$_{H,H}$ = 2 Hz, 2H, H4/H5), 5.38-5.28 (m, 4H, 2 × benzylic CH$_2$), 3.74 (s, 6H, 2 × CH$_3$).

$^{13}$C NMR (125.75MHz, CD$_3$CN) for (syn-67$^+$): $\delta$ 139.50 (C2), 135.24 (C1'/C2'), 133.40 (C3'/ C6'), 132.61 (C4'/C5'), 126.88 (C4/C5), 126.68 (C4/C5), 109.92 (CN), 103.14 Au(CN)$_4$-, 52.18 (CH$_2$), 39.96 (CH$_3$).

$^1$H NMR (600 MHz, DMSO-$d_6$) for (syn-67$^+$): $\delta$ 7.90 (d, $^3$J$_{H,H}$ = 2, 2H, H4/H5), 7.77 (d, $^3$J$_{H,H}$ = 2, 2H, H4/H5), 7.67 (m, 2H, H3'/H6'), 7.62 (m, 2H, H4'/H5'), 5.49-5.46 (d, $^2$J$_{H,H}$ = 15, 2H, benzylic CH$_2$), 5.39-5.35 (d, $^2$J$_{H,H}$=15, 2H, benzylic CH$_2$), 3.80 (s, 6H, 2 × CH$_3$).
When a DMSO-$d_6$ solution of $\text{syn-67.Au(CN)}_4$ was left to stand for 40 days, a new complex tentatively assigned as $\text{anti-67}^+$ was detected by $^1$H NMR spectroscopy.

$^1$H NMR (600 MHz, DMSO-$d_6$) for ($\text{anti-67}^+$): $\delta$ 8.08 (d, $^3J_{H,H} = 2.5, 2\text{H, H4/H5}$), 7.93 (m, 2H, H4'/H5'), 7.73 (d, $^3J_{H,H} = 2.5, 2\text{H, H4/H5}$), 7.48 (m, 2H, H3'/H6'), 6.37-6.39 (d, $^2J_{H,H} = 15, 2\text{H, benzylic CH}_2$), 5.29-5.32 (d, $^2J_{H,H} = 15, 2\text{H, benzylic CH}_2$), 3.89 (s, 6H, 2 $\times$ CH$_3$).

Microanalysis: Found: C, 32.35; H, 2.33; N, 16.05% $\text{Au}_2\text{C}_{22}\text{H}_{18}\text{N}_{10}$.($\text{CH}_3\text{OH})_{1.2}$ requires C, 32.60; H, 2.69; N, 16.39%.

HRMS (ESI$^+$): Calcd for $\text{AuC}_{18}\text{H}_{18}\text{N}_6^+$ ([M-Au(CN)$_4$]$^+$), m/z 515.1259. Found, m/z 515.1272.

Crystals suitable for X-ray diffraction studies were grown by slow evaporation of an acetonitrile solution of the complex.
The dinuclear dicyanido Au$^{III}$ complex 70·2Br

![Diagram of the complex](image)

A solution of NaCN (5.5 mg, 0.11 mmol) in water (5 mL) was added to a solution of 69·2Br (38 mg, 0.027 mmol) in methanol (15 mL). The mixture was stirred for 3 h at room temperature. After that, the white precipitate was collected, washed with water several times and dried in vacuo to afford 70·2Br as colourless crystals (22 mg, 68%).

$^1$H NMR (600 MHz, DMSO-d$_6$): $\delta$ 7.90 (d, $^3J_{H,H} = 1.5$ Hz, 4H, H4/H5), 7.74 (d, $^3J_{H,H} = 1.5$, 4H, H4/H5), 7.41 (t, $^3J_{H,H} = 8$ Hz, 2H, H5'), 7.40 (s, 2H, H2'), 6.90 (br s, 4H, H4'/H6'), 5.10 (s, 8H, benzylic CH$_2$), 4.02 (s, 12H, 4 × CH$_3$).

$^{13}$C NMR (125.75MHz, DMSO-d$_6$): $\delta$ 149.41 (C2), 135.30 (C1'/C3'), 130.00 (C5'), 128.28 (C4'/C6'), 127.68 (C2'), 126.04 (C4/C5), 124.96 (C4/C5), 102.45 (CN), 52.53 (CH$_2$), 37.77 (CH$_3$).

HRMS (ESI$^+$): Calcd for Au$_2$C$_{36}$H$_{36}$N$_{12}$Br$^+$ ([M-Br]$^+$), m/z 1109.1700. Found, m/z 1109.1730.

Crystals suitable for X-ray diffraction studies were grown by slow evaporation of an acetonitrile solution of the complex.
The Au\textsuperscript{III} Cl\textsubscript{2}(diNHC)\textsubscript{2} complex 45·Cl

![Diagram of the complex]

A solution of LiOAc (80 mg, 1.21 mmol) in DMF (5 mL) added to a mixture of 42·2HCl (99 mg, 0.40 mmol) and KAuCl\textsubscript{4} (75 mg, 0.20 mmol) in DMF (10 mL) at 80 °C. The mixture was then heated to 100 °C and this temperature was maintained for 5 h. The white precipitate that formed was collected by filtration and washed successively with DMF, acetone, and Et\textsubscript{2}O to leave 45·Cl as a white powder (106 mg, 81%).

\textsuperscript{1}H NMR (600 MHz, DMSO-\textit{d}\textsubscript{6}): δ 8.09 (d, \textit{J}_{H,H} = 15.3 Hz, 2H, CHH), 8.03 (d, \textit{J}_{H,H} = 2.1 Hz, 4H, H4/H5), 7.77 (d, \textit{J}_{H,H} = 2.1 Hz, 4H, H4/H5), 6.79 (d, \textit{J}_{H,H} = 15.3 Hz, 2H, CHH), 3.69 (s, 12H, 4× CH\textsubscript{3}).

\textsuperscript{13}C NMR (150.90 MHz, DMSO-\textit{d}\textsubscript{6}): δ146.82 (C2), 124.96 (C4/C5), 123.63 (C4/C5), 63.15 (CH\textsubscript{2}), 37.78 (CH\textsubscript{3}).

Microanalysis: Found: C, 32.88; H, 3.66; N, 17.10% AuC\textsubscript{18}H\textsubscript{24}N\textsubscript{8}Cl\textsubscript{3} requires C, 32.97; H, 3.69; N, 17.09%.

HRMS (ESI\textsuperscript{+}): Calcd for AuC\textsubscript{18}H\textsubscript{24}N\textsubscript{8}Cl\textsubscript{5} [M-Cl]\textsuperscript{+}, \textit{m/z} 619.1166. Found, \textit{m/z} 619.1160.

Crystals suitable for X-ray diffraction studies were grown by diffusion of vapours between neat diethyl ether and a solution of the complex in methanol.
The Au\textsuperscript{III}(diNHC)\textsubscript{2} complex 48·3PF\textsubscript{6}

A solution of KPF\textsubscript{6} (106 mg, 0.58 mmol) in water (3 mL) was added in a solution of 45·Cl complex (106 mg, 0.17 mmol) in CH\textsubscript{3}OH (10 mL). The resulting precipitate was collected by filtration and washed with water (3 mL) and methanol (3 x 3 mL) to leave 48·3PF\textsubscript{6} as a white powder (93 mg, 59%).

\begin{align*}
^{1}\text{H NMR} \ (600 \text{ MHz, DMSO}-d\textsubscript{6}): & \delta \ 8.01 \ (d, \ ^{3}J_{H,H} = 1.8 \text{ Hz}, \ 2\text{H}, \ H4/H5), \ 7.77 \ (d, \ ^{3}J_{H,H} = 1.8 \text{ Hz}, \ 2\text{H}, \ H4/H5), \ 6.84 \ (d, \ ^{2}J_{H,H} = 13.2 \text{ Hz}, \ 2\text{H}, \ CH/H), \ 6.75 \ (d, \ ^{2}J_{H,H} = 13.2 \text{ Hz}, \ 2\text{H}, \ CH/H), \ 3.50 \ (s, \ 12\text{H}, \ 4\times \ CH\textsubscript{3}). \\
^{13}\text{C NMR} \ (150.90 \text{ MHz, DMSO}-d\textsubscript{6}): & \delta \ 146.68 \ (C2), \ 125.16 \ (C4/C5), \ 124.28 \ (C4/C5), \ 63.09 \ (CH\textsubscript{2}), \ 37.83 \ (CH\textsubscript{3}). \\
^{31}\text{P NMR} \ (242.93 \text{ MHz, DMSO}-d\textsubscript{6}): & \delta \ -144.20 \ (\text{sept}, \ ^{1}J_{P,F} = 709.8 \text{ Hz}, \ PF\textsubscript{6}).
\end{align*}

Microanalysis: Found: C, 21.88; H, 2.57; N, 11.43% AuC\textsubscript{18}H\textsubscript{24}N\textsubscript{8}P\textsubscript{3}F\textsubscript{18} requires C, 21.96; H, 2.46; N, 11.38%.

HRMS (ESI\textsuperscript{+}): Calcd for AuC\textsubscript{18}H\textsubscript{24}N\textsubscript{8}P\textsubscript{2}F\textsubscript{12}\textsuperscript{+} \ [M-PF\textsubscript{6}]\textsuperscript{+}, \ m/z \ 839.1073. Found: \ m/z \ 839.1071.

Crystals suitable for X-ray diffraction studies were grown by diffusion of vapours between neat diethyl ether and a solution of the complex in acetonitrile.
The \([\text{Au}^{III}\text{Cl}_2(\text{diNHC})_2]\) complex 46·Cl

A solution of LiOAc (61 mg, 0.92 mmol) in DMF (5 mL) added to a mixture of 43·2HCl (105 mg, 0.40 mmol) and KAuCl₄ (75 mg, 0.20 mmol) in DMF (10 mL) at 80 °C. The mixture was then heated to 110 °C and this temperature was maintained overnight. The white precipitate that formed was collected by filtration and washed successively with DMF, acetone, and Et₂O to leave 46·Cl as a white powder (108 mg, 79%).

\(^1\text{H NMR}\) (600 MHz, DMSO-\(d_6\)):  δ 7.86 (d, \(^3J_{HH} = 2.1\) Hz, 4H, H4/H5), 7.73 (d, \(^3J_{HH} = 2.1\) Hz, 4H, H4/H5), 5.46 (m, 4H, 2 ×CH₂), 4.91 (m, 4H, 2 ×CH₂), 3.35 (s, 12H, 4× CH₃).

\(^1^3\text{C NMR}\) (150.90 MHz, DMSO-\(d_6\)): δ144.58 (C2), 126.47 (C4/C5), 125.13 (C4/C5), 47.64 (CH₂), 38.01 (CH₃).

Microanalysis: Found: C, 35.32; H, 4.33; N, 16.05% \(\text{AuC}_{26}\text{H}_{28}\text{N}_{8}\text{Cl}_{3}\) requires C, 35.13; H, 4.13; N, 16.39%.

HRMS (ESI⁺): Caled for \(\text{AuC}_{26}\text{H}_{28}\text{N}_{8}\text{Cl}_{2}^+ [\text{M-Cl}]^+\), \(m/z\) 647.1479. Found, \(m/z\) 647.1464.

Crystals suitable for X-ray diffraction studies were grown by diffusion of vapours between neat diethyl ether and a solution of the complex in methanol.
The Au\textsuperscript{III}(diNHC)\textsubscript{2} complex 49·3PF\textsubscript{6}

This compound was prepared in the same way as 48·3PF\textsubscript{3} complex, and was obtained in 69% yield.

\textsuperscript{1}H NMR (600 MHz, DMSO-\textit{d}\textsubscript{6}): \(\delta\) 7.84 (d, \(^3J_{\text{H,H}} = 1.8\) Hz, 4H, H4/H5), 7.71 (d, \(^3J_{\text{H,H}} = 1.8\) Hz, 4H, H4/H5), 5.30 (m, 4H, 2 ×CH\textsubscript{2}), 4.93 (m, 4H, 2 ×CH\textsubscript{2}), 3.30 (s, 12H, 4 × CH\textsubscript{3}).

\textsuperscript{13}C NMR (150.90 MHz, DMSO-\textit{d}\textsubscript{6}): \(\delta\) 145.14 (C2), 127.05 (C4/C5), 125.76 (C4/C5), 47.92 (CH\textsubscript{2}), 38.19 (CH\textsubscript{3}).

\textsuperscript{31}P NMR (242.93 MHz, DMSO-\textit{d}\textsubscript{6}): \(\delta\) -144.21 (sept, \(^1J_{\text{P,F}} = 713.3\) Hz, PF\textsubscript{6}).

Microanalysis: Found: C, 23.13, H, 3.30, N; 10.80. C\textsubscript{20}H\textsubscript{28}AuF\textsubscript{18}N\textsubscript{8}P\textsubscript{3}.(H\textsubscript{2}O) requires C, 23.31, H, 2.93, N, 10.88%.

HRMS (ESI\textsuperscript{+}): Calcd for AuC\textsubscript{20}H\textsubscript{28}N\textsubscript{8}P\textsubscript{2}F\textsubscript{12}\textsuperscript{+} [M-PF\textsubscript{6}]\textsuperscript{+}, \textit{m/z} 867.1386. Found, \textit{m/z} 867.1344.

Crystals suitable for X-ray diffraction studies were grown by diffusion of vapours between neat diethyl ether and a solution of the complex in acetonitrile.
The Au\textsuperscript{III}Cl\textsubscript{2}(NHC)\textsubscript{4} complex 47·Cl

A solution of LiOAc (20 mg, 0.30 mmol) in DMF (5 mL) added to a mixture of 44·4HCl (54 mg, 0.083 mmol) and KAuCl\textsubscript{4} (32 mg, 0.083 mmol) in DMF (10 mL) at 80 °C and this temperature was maintained overnight. The white precipitate that formed was collected by filtration and washed successively with DMF, acetone, and Et\textsubscript{2}O to leave 47·Cl as a white powder (32 mg, 48%).

\textsuperscript{1}H NMR (600 MHz, DMSO-\textit{d}_6): \(\delta\) 7.97 (d, \(^3J_{\text{H,H}} = 2.1\) Hz, 4H, H4/H5), 7.68, 7.52 (m, 8H, C\textsubscript{6}H\textsubscript{4}), 7.48 (d, \(^2J_{\text{H,H}} = 12.6\) Hz, 2H, CH/CH), 7.42 (d, \(^3J_{\text{H,H}} = 2.1\) Hz, 4H, H4/H5), 6.78 (d, \(^2J_{\text{H,H}} = 12.6\) Hz, 2H, CH/CH), 5.26 (d, \(^2J_{\text{H,H}} = 15.6\) Hz, 4H, benzylic CH/CH), 5.15 (d, \(^2J_{\text{H,H}} = 15.6\) Hz, 4H, benzylic CH/CH).

\textsuperscript{13}C NMR (150.90 MHz, DMSO-\textit{d}_6): \(\delta\) 145.92 (C2), 134.96 (C1'/C2'), 132.20 (C3'/C6'), 129.70 (C4'/C5'), 125.11 (C4/C5), 123.73 (C4/C5), 62.20 (CH\textsubscript{2}), 52.64 (benzylic CH\textsubscript{2}).

Microanalysis: Found: C, 44.65; H, 3.52; N, 13.83% AuC\textsubscript{30}H\textsubscript{28}N\textsubscript{8}Cl\textsubscript{3} requires C, 44.82; H, 3.51; N, 13.94%.

HRMS (ESI\textsuperscript{+}): Calcd for AuC\textsubscript{30}H\textsubscript{28}N\textsubscript{8}Cl\textsubscript{3}\textsuperscript{+} [M-Cl]\textsuperscript{+}, \textit{m/z} 767.1479. Found, \textit{m/z} 767.1469.

Crystals suitable for X-ray diffraction studies were grown by diffusion of vapours between neat diethyl ether and a solution of the complex in methanol.
The Au\textsuperscript{III}(NHC)\textsubscript{4} complex 50–3PF\textsubscript{3}

This compound was prepared in the same way as 48–3PF\textsubscript{3} complex, and was obtained in 72\% yield.

\textsuperscript{1}H NMR (600 MHz, DMSO–d\textsubscript{6}): δ 7.98 (d, \textsuperscript{3}J\textsubscript{H,H} = 1.8 Hz, 4H, H4/H5), 7.69, 7.56 (m, 8H, C\textsubscript{6}H\textsubscript{4}), 7.44 (d, \textsuperscript{3}J\textsubscript{H,H} = 1.8 Hz, 4H, H4/H5), 6.82 (d, \textsuperscript{2}J\textsubscript{H,H} = 13.2 Hz, 2H, CHH), 6.72 (d, \textsuperscript{2}J\textsubscript{H,H} = 13.2 Hz, 2H, CHH), 5.34 (d, \textsuperscript{2}J\textsubscript{H,H} = 15.3 Hz, 4H, benzylic CHH), 5.00 (d, \textsuperscript{2}J\textsubscript{H,H} = 15.3 Hz, 4H, benzylic CHH).

\textsuperscript{13}C NMR (150.90 MHz, DMSO–d\textsubscript{6}): δ146.21 (C2), 134.86 (C1′/C2′), 132.20 (C3′/C6′), 129.86 (C4′/C5′), 125.86 (C4/C5), 124.21 (C4/C5), 62.24 (CH\textsubscript{2}), 52.32 (benzylic CH\textsubscript{2}).

\textsuperscript{31}P NMR (242.93 MHz, DMSO–d\textsubscript{6}): δ -144.20 (sept, \textsuperscript{1}J\textsubscript{P,F} = 711.5 Hz, PF\textsubscript{6}).

Microanalysis: Found: C, 31.90; H, 2.39; N, 9.73\% AuC\textsubscript{30}H\textsubscript{28}N\textsubscript{8}P\textsubscript{3}F\textsubscript{18} requires C, 31.82; H, 2.49; N, 9.89\%.

HRMS (ESI\textsuperscript{+}): Calcd for AuC\textsubscript{30}H\textsubscript{28}N\textsubscript{8}P\textsubscript{2}F\textsubscript{12}\textsuperscript{+} [M-PF\textsubscript{6}]\textsuperscript{+}, m/z 987.1386. Found, m/z 987.1396.

Crystals suitable for X-ray diffraction studies were grown by diffusion of vapours between neat diethyl ether and a solution of the complex in acetonitrile.
8.3.6 *Au^{II}*-NHC & *Au^{I}/Au^{III}*-NHC complexes

The dinuclear Au^{II} complex 34·2Cl

[Chemical structure image]

Thionyl chloride (6 drops, 53 mg, 0.445 mmol) was added to a solution of Au^{I} complex 11·2Cl (34 mg, 0.032 mmol) in CH_{3}CN (15 mL) and the mixture was stirred overnight at room temperature. The volatiles were removed under reduced pressure and the residue was washed with Et_{2}O several times and dried *in vacuo* to leave 34·2Cl as a yellow solid (31 mg, 90%).

^{1}H NMR (600 MHz, DMSO-d_{6}): δ 7.95-7.93 (m, 8H, H3’/H6’), 7.63-7.62 (m, 8H, H4’/H5’), 6.74 (s, 8H, H4/H5), 6.12 (d, 2J_{H,H} = 13.8 Hz, 8H, benzylic HCH), 5.33 (d, 2J_{H,H} = 13.8 Hz, 8H, benzylic HCH).

^{13}C NMR (150.90 MHz, DMSO-d_{6}): δ 159.62 (C2), 135.05 (C1’/C2’), 134.00 (C3’/C6’), 130.78 (C4’/C5’), 123.62 (C4/C5), 52.44 (benzylic CH_{2}).

HRMS (ESI^+): Calcd for Au_{2}C_{44}H_{40}N_{8}Cl_{3}^{+} [M-Cl]^+, m/z 1179.1773. Found, m/z 1179.1766.

Crystals suitable for X-ray diffraction studies were grown by diffusion of vapours between neat diethyl ether and a solution of the complex in methanol.
The dinuclear Au\textsuperscript{II} complex 35·2Br

A solution of bromine (6.0 µL, 0.116 mmol) in CH\textsubscript{3}CN (5 mL) was added to a solution of Au\textsuperscript{I} complex 11·2Br (37 mg, 0.032 mmol) in CH\textsubscript{3}CN (10 mL) and the mixture was stirred overnight at room temperature. The volatiles were removed under reduced pressure and the residue was washed with Et\textsubscript{2}O several times and dried \textit{in vacuo} to leave 35·2Br as a yellow solid (30 mg, 62 %).

\textsuperscript{1}H NMR (600 MHz, DMSO-\textit{d}\textsubscript{6}): \( \delta \) 7.96-7.95 (m, 8H, H3'/H6'), 7.63-7.62 (m, 8H, H4'/H5'), 6.73 (s, 8H, H4/H5), 6.07 (d, \( ^2J_{H,H} = 13.8 \) Hz, 8H, benzylic HCH), 5.28 (d, \( ^2J_{H,H} = 13.8 \) Hz, 8H, benzylic HCH).

\textsuperscript{13}C NMR (150.90 MHz, DMSO-\textit{d}\textsubscript{6}): \( \delta \) 159.12 (C2), 134.56 (C1'/C2'), 133.52 (C3'/C6'), 130.30 (C4'/C5'), 123.13 (C4/C5), 51.95 (benzylic CH\textsubscript{2}).

HRMS (ESI\textsuperscript{+}): Calcd for Au\textsubscript{2}C\textsubscript{44}H\textsubscript{40}N\textsubscript{8}Br\textsubscript{3} \textsuperscript{+} [M-Br]\textsuperscript{+}, \( m/z \) 1311.0257. Found, \( m/z \) 1311.0231.

Crystals suitable for X-ray diffraction studies were grown by diffusion of vapours between neat diethyl ether and a solution of the complex in methanol.
The dinuclear Au\textsuperscript{II} complex 36·2PF\textsubscript{6}

A solution of iodine (6.0 mg, 0.024 mmol) in CH\textsubscript{3}CN (5 mL) was added to a solution of Au\textsuperscript{I} complex 11·2PF\textsubscript{6} (25.8 mg, 0.022 mmol) in CH\textsubscript{3}CN (10 mL) and the mixture was stirred overnight at room temperature. The volatiles were removed under reduced pressure and the residue was washed with Et\textsubscript{2}O several times and dried \textit{in vacuo} to leave 36·2PF\textsubscript{6} as a brown solid (29 mg, 85 %).

\textsuperscript{1}H NMR (600 MHz, DMSO-\textit{d}\textsubscript{6}): \(\delta\) 7.94-7.96 (m, 8H, H3'/H6'), 7.61-7.63 (m, 8H, H4'/H5'), 6.71 (s, 8H, H4/H5), 5.96 (d, \(\text{\textit{J}}_{\text{H,H}} = 14.4\text{ Hz}, 8\text{H}, \text{benzylic HCH}), 5.18 (d, \(\text{\textit{J}}_{\text{H,H}} = 14.4\text{ Hz}, 8\text{H}, \text{benzylic HCH}).

\textsuperscript{13}C NMR (150.90 MHz, DMSO-\textit{d}\textsubscript{6}): \(\delta\) 157.99 (C2), 134.53 (C1'/C2'), 133.55 (C3'/C6'), 130.29 (C4'/C5'), 123.08 (C4/C5), 51.97 (benzylic CH\textsubscript{2}).

HRMS (ESI\textsuperscript{+}): Calcd for Au\textsubscript{2}C\textsubscript{44}H\textsubscript{40}N\textsubscript{8}I\textsubscript{2}PF\textsubscript{6}\textsuperscript{+} [M-PF\textsubscript{6}]\textsuperscript{+}, \(m/z\) 1473.0438. Found, \(m/z\) 1473.0269; Calcd for Au\textsubscript{2}C\textsubscript{44}H\textsubscript{40}N\textsubscript{8}I\textsuperscript{+} [M-2PF\textsubscript{6}-I]\textsuperscript{+}, \(m/z\) 1201.1752. Found, \(m/z\) 1201.1732.

Crystals suitable for X-ray diffraction studies were grown by slow evaporation of an acetone solution of the complex.
Thionyl chloride (5 drops, 50 mg, 0.42 mmol) was added to a solution of AuI complex 12·2Cl (30 mg, 0.028 mmol) in CH₃CN (15 mL) and the mixture was stirred overnight at room temperature. The volatiles were removed under reduced pressure and the residue was washed with Et₂O several times and dried in vacuo to leave 37·2Cl as a yellow solid (25 mg, 87 %).

¹H NMR (600 MHz, DMSO-d₆): δ 7.47 (s, 8H, H4/H5), 7.22-7.20 (d, ³J₃,₃ = 12 Hz, 8H, H4'/H6'), 6.89 (t, ³J₃,₃ = 7.2 Hz, 4H, H5'), 5.80 (s, 4H, H2'), 5.43-5.34 (m, 16H, 8 × benzyllic CH₂).

¹H NMR (600 MHz, methanol-d₄ at -10 °C): δ 7.47 (s, 4H, H4/H5), 7.26 (s, 4H, H4/H5), 7.30 (d, ³J₃,₃ = 7.5 Hz, 4H, H4'/H6'), 7.18 (d, ³J₃,₃ = 7.5 Hz, 4H, H4'/H6'), 7.04 (t, ³J₃,₃ = 7.5 Hz, 4H, H5'), 6.00 (s, 4H, H2'), 5.60 (d, ²J₃,₃ = 16.5 Hz, 4H, benzyllic CH₂), 5.23 (d, ²J₃,₃ = 16.5 Hz, 4H, benzyllic CH₂), 5.43-5.36 (AB, ²J₃,₃ = 16.5 Hz, 8H, benzyllic CH₂).

¹³C NMR (150.90 MHz, DMSO-d₆): Not seen (C2), δ 136.50 (C1'/C3'), 128.07 (C5'), 126.22 (C4'/C6'), 124.36 (C4/C5), 122.39 (C2'), 52.75 (CH₂).
\(^{13}\)C NMR (150.90 MHz, methanol-d\(_4\)): \(\delta\) 186.42, 155.99 (C2), 138.81, 136.96 (C1'/C3'), 127.81 (C5') 126.45, 127.61 (C4'/C6'), 124.17, 129.98 (C4/C5), 124.33 (C2'), 54.35, 54.65 (CH\(_2\)).

HRMS (ESI\(^+\)): Calcd for \(\text{Au}_2\text{C}_{44}\text{H}_{40}\text{N}_8\text{Cl}_3^+\) [M-Cl]\(^+\), \(m/z\) 1179.1773. Found, \(m/z\) 1179.1740.

Crystals suitable for X-ray diffraction studies were grown by diffusion of vapours between neat diethyl ether and a solution of the complex in methanol.

**The Au\(^I\)/Au\(^{III}\) complex 38·2Br**

A solution of bromine (6.0 µL, 0.116 mmol) in CH\(_3\)CN (5 mL) was added to a solution of Au\(^I\) complex 12·2Br (54 mg, 0.046 mmol) in CH\(_3\)CN (10 mL) and the mixture was stirred overnight at room temperature. The volatiles were removed under reduced pressure and the residue was washed with Et\(_2\)O several times and dried *in vacuo* to leave 38·2Br as a yellow solid (60 mg, 98 %).

\(^1\)H NMR (600 MHz, DMSO-d\(_6\)): \(\delta\) 7.49 (s, 8H, H4/H5), 7.19-7.18 (d, \(^3\)J\(_{H,H}\) = 8.4 Hz, 8H, H4'/H6'), 6.80 (t, \(^3\)J\(_{H,H}\) = 7.8 Hz,4H, H5'), 5.89 (s, 4H, H2'), 5.39-5.38 (m, 16H, benzylic CH\(_2\)).
$^{13}$C NMR (150.90 MHz, DMSO-$d_6$): 166.71 (C2), $\delta 136.18$ (C1'/C3'), 128.01 (C5'), 126.16 (C4'/C6'), 124.63 (C4/C5), 122.93 (C2'), 52.72 (CH$_2$).

HRMS (ESI$^+$): Calcd for Au$_2$C$_{44}$H$_{40}$N$_8$Br$_3^+$ [M-Br]$^+$, $m/z$ 1311.0257. Found, $m/z$ 1311.0209.

Crystals suitable for X-ray diffraction studies were grown by diffusion of vapours between neat diethyl ether and a solution of the complex in methanol.
8.4 X-Ray crystal structure determination

Diffraction data were obtained and refined by Brian Skelton and Alexandre Sobolev.

Crystallographic data were collected at 100(2) K on an Oxford Diffraction Xcalibur or Gemini diffractometer using Mo Kα radiation or Cu Kα radiation. Following analytical absorption corrections and solution by direct methods, the structures were refined against \( F^2 \) with full-matrix least-squares using the program SHELXL-2014. All hydrogen atoms were added at calculated positions and refined by use of riding models with isotropic displacement parameters based on those of the parent atoms. Except for those atoms mentioned below, anisotropic displacement parameters were employed throughout for the non-hydrogen atoms.

In 33, the imidazolylidene ring on one of the molecules is rotationally disordered over two sets of sites with refined occupancies of 0.580(5) and its complement. For the structure of 34·2Cl, one solvent was modelled as a methanol molecule. For 35·2Br, the solvent was modelled as one molecule of ether, with its site occupancy constrained to 0.5 from trial refinement and considerations of intermolecular contacts, and one molecule of methanol. For 37·2Cl, the anion was modelled as being one chloride with full occupancy and one chloride disordered over three sites with site occupancies constrained to 0.5,0.25,0.25 after trial refinement, these being disordered with solvent water and methanol molecules at similar sites. One additional water molecule and a methanol molecule were refined with full occupancies. For the structure of 38·2Br, one bromide ion was modelled as being disordered over two sites with occupancies refined to 0.857(8) and its complement.
For the structure of 47-CI(MeOH)$_3$·$\delta$, one chlorido ligand was modelled as being disordered with a molecule of methanol with site occupancies constrained to 0.75 and 0.25 from trial refinement and as required for charge balance. Remaining solvent molecules were modelled as three molecules of methanol situated on a crystallographic mirror plane. Geometries and displacement parameters of the solvent were restrained to reasonable values. Solvent hydrogen atoms were not included in the model. For the structure of 48-3PF$_6$(MeCN)$_2$, the solvent acetonitrile molecule was found to be disordered over two sites with the methyl atom common to both components. In 49-3PF$_6$(MeCN)$_2$, the ligand and one hexafluorophosphate anion are both disordered over two sets of sites with occupancies refined to 0.765(4) and its complement after trial refinement showed no significant differences in the refined values. The atoms of the minor component of the cation were refined with isotropic displacement parameters. The remaining hexafluorophosphate anion was modelled as being rotationally disordered with site occupancies were constrained to 0.5 after trial refinement. The solvent was modelled as acetonitrile, disordered over two sets of sites. For the structure of 50-3PF$_6$(MeCN)$_3$, the fluorine atoms of two hexafluorophosphate anions were modelled as being disordered over two sites; hexafluorophosphate anion (1) where site occupancies were refined to 0.75(2) and its complement and hexafluorophosphate anion (3) where fluorine occupancies were constrained to 0.5 after trial refinement. For 64-Au(CN)$_0.5$(Br)$_0.5$, The bromide ion modelled as being disordered about a crystallographic inversion centre.

For 86-Cl both imidazole-thione ligands were modelled as being disordered over two sets of sites with occupancies constrained to 0.5 after trial refinement. Geometries
were restrained to ideal values. The chloride anion was also modelled as being disordered over two sites with occupancies refined to 0.75(1) and its complement. For 88·2Cl, the cation was modelled as being disordered over two sets of sites with site occupancies refined to 0.823(3) and its complement. The minor component was refined with some geometry restrained to ideal values and with most atoms with isotropic displacement parameters. For 89·2PF₆, the PF₆⁻ anion was modelled as being disordered over two sets of sites with occupancies constrained to 2/3 and 1/3 after trial refinement. For 90.PF₆ the anion/solvent was modelled as mixed PF₆⁻, AuCl₂⁺, Cl⁻ and water molecules disordered over three sites. One site consists of AuCl₂⁺ disordered with two Cl⁻ ions, the second site of PF₆⁻ anion disordered with water and the third site as PF₆⁻ disordered over two sites. The sites occupancies were refined to 0.611(2) for the major component and its complement for the minor component.
8.5 References


Appendices

Appendix A: NMR Spectra of complexes

Figure A1. $^1$H NMR spectrum of 34·2Cl in DMSO-$d_6$ at 600.13 MHz.
Figure A2. $^{13}$C NMR spectrum of 34-2Cl in DMSO-$d_6$ at 150.9 MHz.
Figure A3. $^1$H NMR spectrum of 35·2Br in DMSO-$d_6$ at 600.13 MHz.
Figure A4. $^{13}$C NMR spectrum of 35·2Br in DMSO-$d_6$ at 150.9 MHz.
Figure A5. $^1$H NMR spectrum of 36·2PF$_6$ in DMSO-$d_6$ at 600.13 MHz.
Figure A6. $^{13}$C NMR spectrum of 36·2PF$_6$ in DMSO-$d_6$ at 150.9 MHz.
Figure A7. $^1$H NMR spectrum of 37·2Cl (600.13 MHz, methanol-$d_4$) at 0 °C.
Figure A8. $^{13}$C NMR spectrum of 37·2Cl in methanol-$d_4$ at 150.9 MHz.
Figure A9. $^1$H NMR spectrum of 37·2Cl in DMSO-$d_6$ at 600.13 MHz.
Figure A10. $^{13}$C NMR spectrum of $37\cdot 2\text{Cl}$ in DMSO-$d_6$ at 150.9 MHz.
Figure A11. $^1$H NMR spectrum of 38·2Br in DMSO-$d_6$ at 600.13 MHz.
Figure A12. $^{13}$C NMR spectrum of 38·2Br in DMSO-$d_6$ at 150.9 MHz.
Figure A13. $^1$H NMR spectrum of 45·Cl in DMSO-$d_6$ at 600.13 MHz.
Figure A14. $^{13}$C NMR spectrum of 45·Cl in DMSO-$d_6$ at 125.77 MHz.
Figure A15. $^1$H NMR spectrum of 48·3PF$_6$ in DMSO-$d_6$ at 600.13 MHz.
Figure A16. $^{13}$C NMR spectrum of 48-3PF$_6$ in DMSO-$d_6$ at 150.90 MHz.
Figure A17. $^1$H NMR spectrum of 46·Cl in DMSO-$d_6$ at 600.13 MHz.
Figure A18. $^{13}$C NMR spectrum of 46·Cl in DMSO-$d_6$ at 150.90 MHz.
Figure A19. $^1$H NMR spectrum of 49·3PF$_6$ in DMSO-$d_6$ at 600.13 MHz.
Figure A20. $^{13}$C NMR spectrum of 49-3PF$_6$ in DMSO-$d_6$ at 150.90 MHz.
Figure A21. $^1$H NMR spectrum of 47·Cl in DMSO-$d_6$ at 600.13 MHz.
Figure A22. $^{13}$C NMR spectrum of 47·Cl in DMSO-$d_6$ at 150.90 MHz.
Figure A23. $^1$H NMR spectrum of 50·3PF$_6$ in DMSO-$d_6$ at 600.13 MHz.
**Figure A24.** $^{13}$C NMR spectrum of 50·3PF$_6$ in DMSO-$d_6$ at 150.90 MHz.
Figure A25. $^1$H NMR spectrum of 60·Br in DMSO-$d_6$ at 500.10 MHz.
$^{13}$C-NMR (DMSO-$d_6$, 125.75 MHz)

Figure A26. $^{13}$C NMR spectrum of 60·Br in DMSO-$d_6$ at 125.75 MHz.
Figure A27. $^1$H NMR spectrum of 61 in DMSO-$d_6$ at 600.13 MHz.
Figure A28. $^{13}$C NMR spectrum of 61 in DMSO-$d_6$ at 125.75 MHz.
Figure A29. $^1$H NMR spectrum of 63·Br in DMSO-$d_6$ at 500.10 MHz.
Figure A30. $^{13}$C NMR spectrum of 63·Br in DMSO-$d_6$ at 125.75 MHz.
Figure A31. $^1$H NMR spectrum of 64·AuBr$_4$ in DMSO-$d_6$ at 600.13 MHz.
Figure A32. $^{13}$C NMR spectrum of $\text{64} \cdot \text{AuBr}_4$ in DMSO-$d_6$ at 150.90 MHz.
Figure A33. $^1$H NMR spectrum of $\text{syn-67} \cdot \text{Au(CN)}_4$ in DMSO-$d_6$ at 500.10 MHz.
Figure A34. $^{13}$C NMR spectrum of syn-67·Au(CN)$_4$ in CD$_3$CN at 125.75 MHz.
Figure A35. $^1$H NMR spectrum of 70·2Br in DMSO-$d_6$ at 500.10 MHz.
Figure A36. $^{13}$C NMR spectrum of $70\cdot2\text{Br}$ in DMSO-$d_6$ at 125.75 MHz.
Figure A37. $^1$H NMR spectrum of 79 in DMSO-$d_6$ at 600.13 MHz.
Figure A38. $^{13}$C NMR spectrum of 79 in DMSO-$d_6$ at 150.90 MHz.
Figure A39. $^1$H NMR spectrum of 31 in DMSO-$d_6$ at 600.13 MHz.
Figure A40. $^{13}$C NMR spectrum of 31 in DMSO-$d_6$ at 150.90 MHz.
Figure A41. $^1$H NMR spectrum of 33 in DMSO-$d_6$ at 500.10 MHz.
Figure A42. $^{13}$C NMR spectrum of 33 in DMSO-$d_6$ at 125.75 MHz.
Figure A43. $^1$H NMR spectrum of 81 in DMSO-$d_6$ at 600.13 MHz.
Figure A44. $^{13}$C NMR spectrum of 81 in DMSO-$d_6$ at 125.75 MHz.
Figure A45. $^1$H NMR spectrum of 85·Cl in DMSO-$d_6$ at 600.13 MHz.
Figure A46. $^{13}$C NMR spectrum of 85·Cl in DMSO-$d_6$ at 150.90 MHz.
Figure A47. $^1$H NMR spectrum of 86·Cl in DMSO-$d_6$ at 500.10 MHz.
Figure A48. $^{13}$C NMR spectrum of 86·Cl in DMSO-$d_6$ at 125.75 MHz.
Figure A49. $^1$H NMR spectrum of 87·2Cl in DMSO-$d_6$ at 500.10 MHz and 65 °C.
Figure A50. $^{13}$C NMR spectrum of 87·2Cl in DMSO-$d_6$ at 150.90 MHz.
Figure A51. $^1$H NMR spectrum of 88·2Cl in DMSO-$d_6$ at 500.10 MHz.
Figure A52. $^{13}$C NMR spectrum of 88-2Cl in DMSO-$d_6$ at 150.90 MHz.
Figure A53. $^1$H NMR spectrum of $89 \cdot 2$PF$_6$ in DMSO-$d_6$ at 500.10 MHz.
Figure A54. $^{13}$C NMR spectrum of 89·2PF$_6$ in DMSO-$d_6$ at 125.75 MHz.
Figure A55. $^1$H NMR spectrum of 90·2PF$_6$ in DMSO-$d_6$ at 500.10 MHz.
Figure A56. $^{13}$C NMR spectrum of 90·2PF$_6$ in DMSO-$d_6$ at 150.90 MHz.
Figure A57. $^1$H NMR spectrum of mixture 91 and 92·Cl in DMSO-$d_6$ at 600.13 MHz and 80 °C.
**Figure A58.** $^{13}$C NMR spectrum of mixture 91 and 92·Cl in DMSO-$d_6$ at 150.90 MHz.
Figure A59. $^1$H NMR spectrum of 93·Cl in DMSO-$d_6$ at 500.10 MHz.
Figure A60. $^{13}$C NMR spectrum of 93·Cl in DMSO-$d_6$ at 125.75 MHz.
Figure A61. $^1$H NMR spectrum of 94·Cl in DMSO-$d_6$ at 600.13 MHz.
Appendix B: Crystal structures

C_{28}H_{34}AuBrN_{4}O. M = 719.47. Monoclinic, Space group P2_1/c (Z = 4); a = 9.71830(10), b = 15.7672(2), c = 16.8138(3) Å, β = 90.2820(10)°, V = 2576.35(6) Å³. Dc = 1.855 Mg/m³. µ = 12.768 mm⁻¹. Crystal size 0.115 x 0.070 x 0.042 mm³. Tmin/max = 0.904/1.00. 2θ_max = 67.35°. restraints / parameters = 4 / 330. Goodness-of-fit on F² = 1.050. R1[I>2σ(I)] = 0.0433, wR2[I>2σ(I)] = 0.1177. R1(all data) = 0.0541, wR2(all data) = 0.1254. Δρ(max/min) = 1.764 and -2.413 e.Å⁻³.

Figure A62. Crystal structure (50% probability level for the displacement ellipsoids) of the cation of 40·Br(H₂O). Selected bond lengths (Å) and angles (°): Au(1)-C(22) 2.039(8), Au(1)-C(42) 2.040(8), C(22)-Au(1)-C(42) 179.4(3).
C$_{36}$H$_{52}$Au$_2$Cl$_6$N$_8$O$_4$. M = 1267.49. Orthorhombic, Space group Pbcn (Z = 4); $a$ = 14.0040(2), $b$ = 20.0894(2), $c$ = 17.7684(2) Å, V = 4998.82(10) Å$^3$. Dc = 1.684 Mg/m$^3$. $\mu$ = 6.226 mm$^{-1}$. Crystal size 0.44 x 0.28 x 0.075 mm$^3$. $T_{\text{min}}$/max = 0.178/0.661. $2\theta_{\text{max}}$ = 31.999°. restraints / parameters = 26 / 278. Goodness-of-fit on $F^2$ = 1.217. $R_1[I>2\sigma(I)] = 0.0499$, $wR_2[I>2\sigma(I)] = 0.1080$. $R_1$(all data) = 0.0632, $wR_2$(all data) = 0.1121. $\Delta\rho$(max/min) = 2.626 and -1.233 e.Å$^{-3}$.

Figure A63. Crystal structure (50% probability level for the displacement ellipsoids) of the cation of 74-Cl$_2$(CH$_3$OH)$_4$. Selected bond lengths (Å) and angles (°): Au(1)-C(42) 2.042(5), Au(1)-C(22) 2.046(5), Au(1)-Cl(2) 2.2792(12), Au(1)-Cl(1) 2.2935(12), C(42)$^1$-Au(1)-C(22) 176.08(19), C(42)$^1$-Au(1)-Cl(2) 90.80(13), C(22)-Au(1)-Cl(2) 90.34(14), C(42)$^1$-Au(1)-Cl(1) 89.25(13), C(22)-Au(1)-Cl(1) 89.54(14), Cl(2)-Au(1)-Cl(1) 179.01(5).
C₃₇H₅₆Au₂Cl₆N₈O₅. M = 1299.53. Triclinic, Space group P\(\overline{1}\) (\(Z = 1\)); \(a = 8.6218(3)\), \(b = 11.6882(5)\), \(c = 12.3962(5)\) Å, \(\alpha = 86.647(4)\), \(\beta = 70.972(4)\), \(\gamma = 87.136(3)\)°, \(V = 1178.30(9)\) Å³. Dc = 1.831 Mg/m³. \(\mu = 6.607\) mm⁻¹. Crystal size 0.544 x 0.259 x 0.104 mm³. \(T_{\text{min/max}} = 0.151/0.548\). \(\theta_{\text{max}} = 30.00°\). restraints / parameters = 15 / 279. Goodness-of-fit on \(F^2\) = 1.075. \(R1[I>2\sigma(I)] = 0.0235\), \(wR2[I>2\sigma(I)] = 0.0573\). \(R1(\text{all data}) = 0.0260\), \(wR2(\text{all data}) = 0.0582\). \(\Delta \rho(\text{max/min}) = 1.742\) and -0.612 eÅ⁻³.

**Figure A64.** Crystal structure (50% probability level for the displacement ellipsoids) of the cation of 75·Cl₂(CH₃OH)₅. Selected bond lengths (Å) and angles (°): Au(1)-C(42) 2.042(3), Au(1)-C(22) 2.046(3), Au(1)-Cl(2) 2.2796(7), Au(1)-Cl(1) 2.2869(8), C(42)-Au(1)-C(22) 178.30(10), C(42)-Au(1)-Cl(2) 89.00(8), C(22)-Au(1)-Cl(2) 89.45(8), C(42)-Au(1)-Cl(1) 89.38(8), C(22)-Au(1)-Cl(1) 92.17(8), Cl(2)-Au(1)-Cl(1) 178.36(2).