Phosphane metal(I) thiolate complexes and their crystal structures

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Thiocarbamide

\[
\begin{align*}
\text{S} & \quad \text{X} \\
\text{RO} & \\
\end{align*}
\]

R = Me, Et and iPr
X = H and CH₃

Gold(I) Compounds

(a) Myocrisin® and (b) Auranofin®

Chemical structures of gold-based DMARDS:
(a) Myocrisin® and (b) Auranofin®

Triphenylphosphanegold(I) Carbonimidothioates

Molecule Assignment

<table>
<thead>
<tr>
<th>Molecule</th>
<th>Assignment</th>
<th>Chemical Shift (ppm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Thioacetamide</td>
<td>¹H – N.H</td>
<td>~ 8.7</td>
</tr>
<tr>
<td>Triphenylphosphine</td>
<td>¹³P – P₃P</td>
<td>-5.2</td>
</tr>
</tbody>
</table>

Aurophilic Interactions

Thiocarbamide

\[
\begin{align*}
\text{H} – \text{N} – \text{H} \\
\text{~ 8.7}  \\
\end{align*}
\]
PrOC(=S)N(H)C₆H₄-4-Me

<table>
<thead>
<tr>
<th>Bond</th>
<th>Bond length (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>C = S</td>
<td>1.6679 (19)</td>
</tr>
<tr>
<td>C – N</td>
<td>1.337 (2)</td>
</tr>
</tbody>
</table>

Ph₃PAu[SC(OEt)=N(Ph)]

Ph₃PAu[SC(OEt)=N(p-tolyl)]

<table>
<thead>
<tr>
<th>Bond</th>
<th>Bond length (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Au – P</td>
<td>2.2561 (7)</td>
</tr>
<tr>
<td>Au – S</td>
<td>2.3171 (7)</td>
</tr>
<tr>
<td>C – S</td>
<td>1.776 (3)</td>
</tr>
<tr>
<td>C = N</td>
<td>1.269 (4)</td>
</tr>
</tbody>
</table>

Ph₃PAu[SC(OEt)=N(p-tolyl)]

Triphenylphosphanegold(I) Carbonimidothioates

R = Me, Et and iPr
X = H and CH₃

Molecular structures of Ph₃PAu[SC(OEt)=N(p-tolyl)]. Displacement ellipsoids are shown at the 50% probability level.
Au⋯O is more stable by ca 12 kcal/mol. At rotation angles = 0 and 360 ° about the C=S bond, Au⋯π is featured while at 180 °, Au⋯O is observed.

Bipodal Thiocarbamide

Chemical structure of 1,4-\{MeOC(=S)N(H)\}C_6H_4H_3CO

Binuclear Phosphanegold(I) Carbonimidothioates

Two intramolecular Au⋯π(aryl) interactions

Binuclear Phosphanegold(I) Carbonimidothioates

Chemical structure of 1,4-\{MeOC(=S)N(H)\}C_6H_4H_3CO

Binuclear Phosphanegold(I) Carbonimidothioates

One Au⋯π(aryl) interaction and one Au⋯O interaction

Binuclear Phosphanegold(I) Carbonimidothioates

R = Et, Ph and Cy
Binuclear Phosphanegold(I) Carbonimidothioates

Two Au···O interactions

Formation of N-H···Cl

R = Me, Et and iPr

Mono- vs Bi-nuclear Phosphanegold(I) Carbonimidothioates

Six Membered Quasi Chelate Ring (CuCl···HNCS)

R = Me, Et and iPr

$2.2854\,\text{Å}$

C-H···π(quasi chelate ring)

ca. 3.5 kcal mol$^{-1}$

$(\text{Ph}_3\text{P})_2\text{Cu}[\text{ROC} (=\text{S})\text{N} (\text{H}) \text{Ph}]\text{Cl}$

$R = \text{Me, Et and } \text{iPr}$

$22/8/2016$
(Ph₃P)₂Cu[ROC(=S)N(H)Ph]Cl

Overlay diagram of Me (red image), Et (green) and iPr (blue). The molecules have been superimposed so the P1-Cu-P2 atoms are overlapped. In this diagram, the inverted molecule of Et has been employed for a better fit.

C-H···π (quasi chelate ring)

Chemical structure of the molecule subjected to DFT-D calculations (BP86-D/def2-TZVP).

Summary

- Au⋯O interactions predominate in mononuclear gold(I) compounds.
- Au⋯π interactions in binuclear gold(I) compounds impart stabilisation to the structure.
- Copper(I) derivatives displayed arene-C-H⋯π(quasi-chelate ring) interactions with stabilisation energy of ca. 3.5 kcal mol⁻¹.

Acknowledgement

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Thank You