SUPPORTING INFORMATION

Backbonding and non-covalent interactions in JohnPhos and polyfluorothiolate complexes of gold(I)

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Calculations concerning the C-S interaction

Table S1. QTAIM calculated parameters for the C-S interaction.

<table>
<thead>
<tr>
<th>Compound</th>
<th>C(para)-S</th>
<th>$\rho_r \text{(r}_{\text{bcp}}$)</th>
<th>$\varepsilon$</th>
<th>DI</th>
</tr>
</thead>
<tbody>
<tr>
<td>[Au(SC$_6$F$_5$)(JPhos)] 1</td>
<td></td>
<td>0.0053</td>
<td>0.8824</td>
<td>0.0282</td>
</tr>
<tr>
<td>[Au(SC$_6$HF$_4$)(JPhos)] 2</td>
<td></td>
<td>0.0055</td>
<td>0.8989</td>
<td>0.0276</td>
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<tr>
<td>[Au(SC$_6$H$_3$F$_2$-3,5)(JPhos)] 3</td>
<td></td>
<td>0.0058</td>
<td>1.3781</td>
<td>0.0365</td>
</tr>
<tr>
<td>[Au(SC$_6$H$_3$F$_2$-2,4)(JPhos)] 4</td>
<td></td>
<td>-</td>
<td>-</td>
<td>0.0012</td>
</tr>
<tr>
<td>[Au(SC$_6$H$_4$F$_2$)(JPhos)] 5</td>
<td></td>
<td>0.0062</td>
<td>1.6709</td>
<td>0.0341</td>
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<tr>
<td>[Au(SC$_6$H$_4$F$_3$)(JPhos)] 6</td>
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<td>0.0057</td>
<td>0.1125</td>
<td>0.0360</td>
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<tr>
<td>[Au(SC$_6$H$_4$F$_4$)(JPhos)] 7</td>
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<td>-</td>
<td>-</td>
<td>0.0255</td>
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<tr>
<td>[Au(SCF$_3$)(JPhos)] 8</td>
<td></td>
<td>0.0062</td>
<td>1.3340</td>
<td>0.0374</td>
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</tbody>
</table>

Note: There is no bond path for the C-S interaction in compounds 4 and 7 so $\rho_r \text{(r}_{\text{bcp}}$) and $\varepsilon$ could not be calculated. $\varepsilon$ is very sensitive to integration errors due to the small electronic density values found for this interaction.
Crystallographic data

Table S2. Crystallographic data

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<tr>
<th>Empirical formula</th>
<th>(<a href="%5Ctext%7BJPh%7D">\text{Au(SC}_2\text{F}_3</a>])</th>
<th>([\text{Au(SC}_2\text{H}_2\text{F}_7\text{F}(\text{JPh})])</th>
<th>(<a href="%5Ctext%7BJPh%7D">\text{Au(SC}_2\text{H}_2\text{F}_7\text{F}-2,4</a>])</th>
<th>(<a href="%5Ctext%7BJPh%7D">\text{Au(SC}_2\text{H}_2\text{F}_7\text{F}-3,5</a>])</th>
<th>(<a href="%5Ctext%7BJPh%7D">\text{Au(SC}_2\text{H}_2\text{F}_7\text{F}-3</a>])</th>
<th>(<a href="%5Ctext%7BJPh%7D">\text{Au(SC}_2\text{H}_2\text{F}_7\text{F}-4</a>])</th>
<th>(<a href="%5Ctext%7BJPh%7D">\text{Au(SCF}_3</a>])</th>
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<td>694.47</td>
<td>676.48</td>
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<td>640.49</td>
<td>622.50</td>
<td>622.50</td>
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<td>298(2) K</td>
<td>130(2) K</td>
<td>130(2) K</td>
<td>130(2) K</td>
<td>130(2) K</td>
<td>100(2) K</td>
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<td>0.71073 Å</td>
<td>0.71073 Å</td>
<td>0.71073 Å</td>
<td>0.71073 Å</td>
<td>0.71073 Å</td>
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<td>Orthorhombic</td>
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<td>Monoclinic</td>
<td>Monoclinic</td>
<td>Triclinic</td>
<td>Monoclinic</td>
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<td>P b c a</td>
<td>P -1</td>
<td>P 21/n</td>
<td>P 21/c</td>
<td>P -1</td>
<td>P 21/n</td>
</tr>
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<td>a = 10.3561(2) Å</td>
<td>a = 9.8864(6) Å</td>
<td>a = 13.3235(8) Å</td>
<td>a = 8.4347(8) Å</td>
<td>a = 11.0004(6) Å</td>
<td>a = 11.1857(4) Å</td>
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<tr>
<td></td>
<td>b = 19.2381(8) Å</td>
<td>b = 19.2100(5) Å</td>
<td>b = 11.9819(7) Å</td>
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<td>b = 17.9915(15) Å</td>
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<td>5193.3(4) Å</td>
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<td>2415.8(4) Å</td>
<td>2467.6(2) Å</td>
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<td></td>
<td>Density (calculated)</td>
<td>1.776 Mg/m³</td>
<td>1.756 Mg/m³</td>
<td>1.744 Mg/m³</td>
<td>1.693 Mg/m³</td>
<td>1.712 Mg/m³</td>
<td>1.676 Mg/m³</td>
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<td>Absorption coefficient</td>
<td>5.856 mm⁻¹</td>
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<td>6.026 mm⁻¹</td>
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<td></td>
<td>F(000)</td>
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<td>2640</td>
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3
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<th>Theta range for data collection</th>
<th>3.682 to 29.496°.</th>
<th>3.730 to 29.624°.</th>
<th>3.410 to 29.447°.</th>
<th>3.444 to 29.329°.</th>
<th>3.418 to 29.496°.</th>
<th>3.428 to 29.503°.</th>
<th>3.445 to 29.575°.</th>
<th>3.561 to 29.336°.</th>
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<td>Index ranges</td>
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<td>-14&lt;=h&lt;=14,</td>
<td>-13&lt;=h&lt;=13,</td>
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<td>-11&lt;=h&lt;=11,</td>
<td>-14&lt;=h&lt;=15,</td>
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<td>36&lt;=l&lt;=33</td>
<td>32&lt;=l&lt;=29</td>
<td>27&lt;=l&lt;=29</td>
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<td>17607</td>
<td>42047</td>
<td>21726</td>
<td>13387</td>
<td>25924</td>
<td>32793</td>
<td>27603</td>
<td>11088</td>
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<tr>
<td>Independent reflections</td>
<td>6213 [R(int) = 0.0492]</td>
<td>6643 [R(int) = 0.0328]</td>
<td>11357 [R(int) = 0.0433]</td>
<td>5974 [R(int) = 0.0343]</td>
<td>6060 [R(int) = 0.0575]</td>
<td>11912 [R(int) = 0.0488]</td>
<td>11810 [R(int) = 0.0365]</td>
<td>5159 [R(int) = 0.0441]</td>
</tr>
<tr>
<td>Completeness to theta = 25.242°</td>
<td>99.7 %</td>
<td>99.7 %</td>
<td>99.7 %</td>
<td>99.7 %</td>
<td>99.7 %</td>
<td>99.8 %</td>
<td>99.7 %</td>
<td>99.7 %</td>
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<td>Refinement method</td>
<td>Full-matrix least-squares on F^2</td>
<td>Full-matrix least-squares on F^2</td>
<td>Full-matrix least-squares on F^2</td>
<td>Full-matrix least-squares on F^2</td>
<td>Full-matrix least-squares on F^2</td>
<td>Full-matrix least-squares on F^2</td>
<td>Full-matrix least-squares on F^2</td>
<td>Full-matrix least-squares on F^2</td>
</tr>
<tr>
<td>Data / restraints / parameters</td>
<td>6213 / 0 / 313</td>
<td>6643 / 0 / 304</td>
<td>11357 / 0 / 571</td>
<td>5974 / 0 / 286</td>
<td>6060 / 0 / 277</td>
<td>11912 / 0 / 553</td>
<td>11810 / 0 / 553</td>
<td>5159 / 0 / 250</td>
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<tr>
<td>Goodness-of-fit on F^2</td>
<td>1.077</td>
<td>1.076</td>
<td>0.972</td>
<td>1.029</td>
<td>1.056</td>
<td>1.064</td>
<td>1.055</td>
<td>1.117</td>
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<tr>
<td>Final R indices [&gt;2sigma(I)]</td>
<td>R1 = 0.0480, wR2 = 0.0795</td>
<td>R1 = 0.0322, wR2 = 0.0586</td>
<td>R1 = 0.0343, wR2 = 0.0551</td>
<td>R1 = 0.0346, wR2 = 0.0764</td>
<td>R1 = 0.0335, wR2 = 0.0686</td>
<td>R1 = 0.0294, wR2 = 0.0495</td>
<td>R1 = 0.0356, wR2 = 0.0748</td>
<td></td>
</tr>
<tr>
<td>R indices (all data)</td>
<td>R1 = 0.0890, wR2 = 0.0921</td>
<td>R1 = 0.0551, wR2 = 0.0658</td>
<td>R1 = 0.0497, wR2 = 0.0646</td>
<td>R1 = 0.0699, wR2 = 0.0667</td>
<td>R1 = 0.0425, wR2 = 0.0829</td>
<td>R1 = 0.0470, wR2 = 0.0765</td>
<td>R1 = 0.0430, wR2 = 0.0546</td>
<td>R1 = 0.0457, wR2 = 0.0798</td>
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<tr>
<td>Extinction coefficient</td>
<td>n/a</td>
<td>n/a</td>
<td>n/a</td>
<td>n/a</td>
<td>n/a</td>
<td>n/a</td>
<td>n/a</td>
<td>n/a</td>
</tr>
<tr>
<td>Largest diff. peak and hole</td>
<td>0.966 and -1.585 e.Å^-3</td>
<td>0.880 and -0.798 e.Å^-3</td>
<td>1.058 and -1.868 e.Å^-3</td>
<td>0.645 and -0.655 e.Å^-3</td>
<td>1.673 and -1.847 e.Å^-3</td>
<td>1.320 and -1.925 e.Å^-3</td>
<td>0.830 and -1.012 e.Å^-3</td>
<td>1.937 and -1.358 e.Å^-3</td>
</tr>
</tbody>
</table>
Theoretical-experimental correlations

$^{31}$P NMR and DI

As expected, the $^{31}$P{${}_1^1$H} NMR spectra of all 8 compounds examined exhibit a single resonance signal. One of the aims of this work was to explore the relationship of the corresponding chemical shift $\delta^{^{31}}$P with the group electronegativity of the fluorinated thiols to assess the different trans effect of each ligand which is ultimately due to the electronegativity of the F atom. A more fluorinated thiolate is expected to attract more electrons from the S-Au-P system by decreasing the $\sigma$ basicity of sulphur. This situation gives place to an unshielded phosphorus atom in trans position. Unfortunately, compounds 1-5 and 8 have practically the same value of chemical shifts, whereas compounds 6 [Au(SC$_6$H$_4$F-3)(JPhos)] and 7 [Au(SC$_6$H$_4$F-4)(JPhos)], present two larger values of $\delta$. Since NMR cannot give us detailed information on the difference in chemical bonding in these compounds, we decided to use quantum chemical topology to get insights about this issue as reported in the main body of the paper.

Table S3. $^{31}$P chemical shifts for the compounds addressed in this investigation

<table>
<thead>
<tr>
<th>Number</th>
<th>Compound</th>
<th>$\delta^{^{31}}$P (ppm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>[Au(SC$_6$F$_5$)(JPhos)]</td>
<td>62.88</td>
</tr>
<tr>
<td>2</td>
<td>[Au(SC$_6$HF$_4$)(JPhos)]</td>
<td>62.83</td>
</tr>
<tr>
<td>3</td>
<td>[Au(SC$_6$H$_3$F$_2$-3,5)(JPhos)]</td>
<td>63.48</td>
</tr>
<tr>
<td>4</td>
<td>[Au(SC$_6$H$_3$F$_2$-2,4)(JPhos)]</td>
<td>63.08</td>
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<tr>
<td>5</td>
<td>[Au(SC$_6$H$_4$F$_2$)(JPhos)]</td>
<td>63.16</td>
</tr>
<tr>
<td>6</td>
<td>[Au(SC$_6$H$_4$F-3)(JPhos)]</td>
<td>68.31</td>
</tr>
<tr>
<td>7</td>
<td>[Au(SC$_6$H$_4$F-4)(JPhos)]</td>
<td>68.59</td>
</tr>
<tr>
<td>8</td>
<td>[Au(SCF$_3$)(JPhos)]</td>
<td>61.75</td>
</tr>
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</table>

As stated in the manuscript, variations in the Au-S delocalization index are small, but it is still interesting to observe the relation between $^{31}$P-NMR chemical shift and the DI between gold and sulphur (reported Table 1) that is shown in Figure S1. This relation establishes the trans influence tendencies of these thiolate ligands, i.e. the larger the electronic density in the Au-S fragment, the larger the unshielding of the trans phosphorus atom.

![Figure S1. Relation between the delocalization index between the gold and the sulphur atom and the chemical shift of $^{31}$P.](image-url)
**Au-C distance and p-backdonation**

The Au-C distance and the Au-S ellipticity present a good correlation for the three monofluorinated compounds. This could mean that a larger $\pi$ electronic density in the Au-S bond is related to a weaker Au-C interaction. Unfortunately, this trend is not clear for the other compounds probably due to packing and competence of other weak contacts.

*Figure S2. Relation between the ellipticity of the Au-S bond critical point and the Au-$\pi$ interaction distance.*
NMR Spectra.

Nuclear magnetic resonance spectra, $^1$H-NMR, $^{13}$C, $^{19}$F and $^{31}$P($^1$H), were recorded on a 9.4 T Varian VNMRS spectrometer. Chemical shifts are in ppm relative to internal TMS $\delta = 0$ ($^1$H, $^{13}$C) and to external references of CFCl$_3$ (for $^{19}$F) and H$_3$PO$_4$ (for $^{31}$P) at 0 ppm. All spectra were obtained using acetone-d$_6$ as solvent at 25 °C.

Note 1: $^1$H-NMR spectra display three signals corresponding to solvent, DHO and H$_2$O between 1.8 and 2.6 ppm

**Compound 1.** [Au(SC$_6$F$_5$)(PC$_{20}$H$_{27}$)].

$^1$H-NMR
\(^{19}\)F-NMR

\(^{13}\)C-NMR
Compound 2. [Au(SC₆H₄-4)(PC₂₀H₂₇)].

$^{31}$P-NMR
$^{19}$F-NMR

$^{13}$C-NMR
Compound 3. [Au(SC₆H₄F₂-3,5)(PC₂₀H₂₇)].

$^1$H-NMR
$^{19}$F-NMR

$^{13}$C-NMR
Compound 4. $[\text{Au(SC}_6\text{H}_3\text{F}_2-2,4)(\text{PC}_{20}\text{H}_{27})]$  
${}^1\text{H-NMR}$
**Compound 5.** [Au(SC₆H₄F-2)(PC₂₀H₂₇)].

**1H-NMR**
**31P-NMR**

**Compound 6.** \([\text{Au}(\text{SC}_6\text{H}_4\text{F}-3)(\text{PC}_{20}\text{H}_{27})]\).

**1H-NMR**
Note 2: $^{19}$F NMR spectra of compound 5 shows a residual secondary signal probably because of a slow decomposition of the product in solution.
Compound 7. [Au(SC₆H₄F-4)(PC₂₀H₂₇)].

¹H-NMR

¹⁹F-NMR
Compound 8. [Au(SCF₃)(PC₂₀H₂₇)].

$^1$H-NMR

$^{19}$F-NMR
$^{13}$C-NMR

$^{31}$P