ELECTRONIC SUPPLEMENTARY INFORMATION

Selective formation of a two-dimensional coordination polymer based on a tridentate phospholane ligand and gold(I)

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1) Experimental Details

4-Bromo-2,6-diethylaniline

\[
\begin{align*}
\text{H NMR (CDCl}_3, 400.13 \text{ MHz): } & \delta = 7.03 (s, 2H, H^4), 3.56 (s, 2H, H^1), 2.41 (q, ^3J_{HH} = 7.5 \text{ Hz}, 4H, H^6), \\
& 1.19 \text{ ppm (t, } ^3J_{HH} = 7.6 \text{ Hz, } 6H, H^7). \\
\text{C}^{13}{\text{H}} \text{ NMR (CDCl}_3, 100.16 \text{ MHz): } & \delta = 140.7 (s, C^2), 129.6 (s, C^3), 128.4 (s, C^4), 110.1 (s, C^5), 24.1 (s, C^6), 12.7 \text{ ppm (s, C}^7). 
\end{align*}
\]

5-Bromo-1,3-diethyl-2-iodobenzene

\[
\begin{align*}
\text{H NMR (CDCl}_3, 400.13 \text{ MHz): } & \delta = 7.15 (s, 2H, H^3), 2.73 (q, ^3J_{HH} = 7.5 \text{ Hz}, 4H, H^5), \\
& 1.18 \text{ ppm (t, } ^3J_{HH} = 7.4 \text{ Hz, } 6H, H^6). \\
\text{C}^{13}{\text{H}} \text{ NMR (CDCl}_3, 100.16 \text{ MHz): } & \delta = 148.8 (s, C^2), 128.7 (s, C^3), 122.6 (s, C^4), 105.4 (s, C^5), 35.3 (s, C^6), 14.5 \text{ ppm (s, C}^7). 
\end{align*}
\]

4-Bromo-2,6-diethylbenzaldehyde

\[
\begin{align*}
\text{H NMR (CDCl}_3, 400.13 \text{ MHz): } & \delta = 7.15 (s, 2H, H^3), 2.73 (q, ^3J_{HH} = 7.5 \text{ Hz}, 4H, H^5), \\
& 1.18 \text{ ppm (t, } ^3J_{HH} = 7.4 \text{ Hz, } 6H, H^6). \\
\text{C}^{13}{\text{H}} \text{ NMR (CDCl}_3, 100.16 \text{ MHz): } & \delta = 148.8 (s, C^2), 128.7 (s, C^3), 122.6 (s, C^4), 105.4 (s, C^5), 35.3 (s, C^6), 14.5 \text{ ppm (s, C}^7). 
\end{align*}
\]
\textbf{H NMR (CDCl}_3, 400.13 \text{ MHz}): \delta = 10.52 (s, 1H, H\textsuperscript{1}), 7.28 (s, 2H, H\textsuperscript{4}), 2.93 (q, J_{HH} = 7.5 \text{ Hz}, 4H, H\textsuperscript{6}), 1.24 \text{ ppm (t, J_{HH} = 7.6 \text{ Hz}, 6H, H\textsuperscript{7}).}

\textbf{13C\textsuperscript{1}H} NMR (CDCl}_3, 100.16 \text{ MHz}): \delta = 192.3 (s, C\textsuperscript{1}), 149.1 (s, C\textsuperscript{3}), 131.0 (s, C\textsuperscript{4}), 130.3 (s, C\textsuperscript{2}), 127.8 (s, C\textsuperscript{5}), 26.4 (s, C\textsuperscript{6}), 16.1 \text{ ppm (s, C\textsuperscript{7}).}

\textbf{1,3,5-Tris[(E)-4-bromo-2,6-diethyl]styrly]benzene (1a)}

\textbf{H NMR (CDCl}_3, 400.13 \text{ MHz}): \delta = 7.53 (s, 3H, H\textsuperscript{1}), 7.25 (s, 6H, H\textsuperscript{9}), 7.16 (d, J_{HH} = 16.0 \text{ Hz, 3H, H\textsuperscript{4}}), 6.62 (d, J_{HH} = 16.0 \text{ Hz, 3H, H\textsuperscript{5}}), 2.70 (q, J_{HH} = 8.0 \text{ Hz, 12H, H\textsuperscript{7}}), 1.20 \text{ ppm (t, J_{HH} = 8.0 \text{ Hz, 18H, H\textsuperscript{8}).}

\textbf{13C\textsuperscript{1}H} NMR (CDCl}_3, 100.16 \text{ MHz}): \delta = 144.6 (s, C\textsuperscript{6}), 138.1 (s, C\textsuperscript{2}), 135.0 (s, C\textsuperscript{5}), 133.9 (s, C\textsuperscript{3}), 128.8 (s, C\textsuperscript{9}), 126.5 (s, C\textsuperscript{10}), 123.6 (s, C\textsuperscript{1}), 121.2 (s, C\textsuperscript{10}), 26.8 (s, C\textsuperscript{7}), 15.9 \text{ ppm (s, C\textsuperscript{8}).}

\textbf{Single-crystal X-ray structure determination:}

The data were collected on a Gemini diffractometer (Rigaku Inc.) using Mo-K\textsubscript{α} radiation (\(\lambda = 71.073 \text{ pm}\)) and \(\omega\)-scan rotation. The structure solution was performed with SHELXS-2013\textsuperscript{[E]} (direct method). Anisotropic refinement of all non-hydrogen atoms was performed with SHELXL-2018\textsuperscript{[C]}. All H atoms were located on difference Fourier maps calculated at the final stage of the structure refinement. CCDC 1861124 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge via https://summary.ccdc.cam.ac.uk/structure-summary-form (or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44)1223-336-033; or deposit@ccdc.cam.uk).

\textbf{Table 1: Crystallographic data of 1,3,5-tris[(E)-4-bromo-2,6-diethyl]styrly]benzene}

\begin{tabular}{|l|}
\hline
\textbf{Empirical formula} & C\textsubscript{42}H\textsubscript{45}Br\textsubscript{3} \\
\textbf{Formula weight} & 789.51 \\
\textbf{Temperature} & 130(2) K \\
\textbf{Wavelength} & 71.073 pm \\
\textbf{Crystal system} & Monoclinic \\
\textbf{Space group} & C\textsubscript{2}/c \\
\textbf{Unit cell dimensions} & a = 2861.00(8) pm \hspace{1cm} \alpha = 90\degree \\
\hline
\end{tabular}
b = 1558.71(3) pm \quad \beta = 96.537(2)^\circ
\c = 1621.90(3) pm \quad \gamma = 90^\circ

Volume 7.1858(3) nm³
Z 8
Density (calculated) 1.460 Mg/m³
Absorption coefficient 3.397 mm⁻¹
F(000) 3216
Crystal size 0.5 x 0.35 x 0.07 mm³
Theta range for data collection 2.516 to 30.507°
Index ranges -40 ≤ h ≤ 40, -22 ≤ k ≤ 21, -23 ≤ l ≤ 23
Reflections collected 64468
Independent reflections 10973 [R(int) = 0.0705]
Completeness to theta = 25.242° 99.9 %
Absorption correction Semi-empirical from equivalents
Max. and min. transmission 1 and 0.49805
Refinement method Full-matrix least-squares on F²
Data / restraints / parameters 10973 / 0 / 586
Goodness-of-fit on F² 1.014
Final R indices [I>2sigma(I)] R1 = 0.0447, wR2 = 0.1000
R indices (all data) R1 = 0.0928, wR2 = 0.1237
Largest diff. peak and hole 1.521 and -1.022 e·Å⁻³

1,3,5-Tris[(E)-(4-phospholano-2,6-diethyl)styryl]benzene (1)

1H NMR (CDCl₃, 400.13 MHz): δ = 7.42 (s, 3H, H¹), 7.15 (d, JHH = 16.8 Hz, 3H, H⁴), 7.05 (d, JHH = 6.8 Hz, 6H, H⁶), 6.56 (d, JHH = 16.8 Hz, 3H, H³), 2.66 (q, JHH = 7.5 Hz, 12H, H⁷), 1.97 – 1.68 (m, 24H, H¹¹+H¹²), 1.40 ppm (t, JHH = 7.5 Hz, 18H, H⁸).
$^1$C($^1$H) NMR (CDCl$_3$, 100.16 MHz): $\delta = 142.1$ (d, $^3J_{CP} = 5.2$ Hz, C$^6$), 140.7 (d, $^3J_{CP} = 21.9$ Hz, C$^{10}$), 138.3 (s, C$^3$), 135.2 (s, C$^5$), 133.4 (s, C$^2$), 128.1 (d, $^3J_{CP} = 15.6$ Hz, C$^9$), 127.0 (s, C$^1$), 123.3 (s, C$^1$), 27.9 (d, $^2J_{CP} = 3.5$ Hz, C$^{12}$), 27.1 – 27.0 (m, C$^7$+C$^{11}$), 15.4 ppm (s, C$^8$).

$^{31}$P($^1$H) NMR (CDCl$_3$, 161.98 MHz): $\delta = –16.8$ ppm (s).

Two-dimensional [M:L] 1:1 coordination polymer from [AuCl(tht)] and 1,3,5-tris([E]-4-phospholano-2,6-diethyl)styryl]benzene – Poly[μ-1,3,5-tris([E]-4-phospholano-2,6-diethyl)styryl]-benzene-κ$^3$P,P,P´,P´´]gold(I) chloride (2)

$^1$H NMR (CD$_2$Cl$_2$, 400.13 MHz): $\delta = 7.53$ (s, 3H, H$^1$), 7.40 (d, $^3J_{HP} = 13.2$ Hz, 6H, H$^9$), 7.27 (d, $^3J_{HH} = 16.7$ Hz, 3H, H$^4$), 6.67 (d, $^3J_{HH} = 16.6$ Hz, 3H, H$^3$), 2.79 (q, $^3J_{HH} = 7.5$ Hz, 12H, H$^7$), 2.54 – 2.02 (m, 24H, H$^{11}$+H$^{12}$), 1.22 ppm (t, $^3J_{HH} = 7.5$ Hz, 18H, H$^8$).

$^{31}$P($^1$H) NMR (CD$_2$Cl$_2$, 161.98 MHz): $\delta = 26.5$ ppm (s).

Single-crystal X-ray structure determination:

The data were collected on a Gemini diffractometer (Rigaku Inc.) using Mo-K$_\alpha$ radiation ($\lambda = 71.073$ pm) and ω-scan rotation. Data reduction was performed with CrysAlis Pro$^{[A]}$ including the program SCALE3 ABSPACK for empirical absorption correction. The structure was solved by dual space methods (SHELXT-2014$^{[B]}$) and the refinement of all non-hydrogen atoms was performed with SHELXL-2018$^{[C]}$. All non-hydrogen atoms were refined with anisotropic thermal parameters. Some parts of the ligand are disordered. All hydrogen atoms were calculated on idealised positions. The crystal was obtained by diffusion of n-hexane into an o-difluorobenzene solution. With a regular structure determination, ten solvent molecules (2.5 for the asymmetric unit) could roughly be located with reduced accuracy as disordered species in 200 pm x 400 pm rectangular sized channels along (010). In this experiment, the electron density of all disordered solvents molecules had been removed with the SQUEEZE$^{[D]}$ routine implemented in PLATON. The squeezed electron density of 647 electrons for the unit cell had been related to 11 poorly defined and diffuse oriented o-difluorobenzene molecules (11 x 58 = 638 electrons), i.e. 2.75 solvent molecules for the asymmetric unit. This is slightly more in comparison with the non-squeezed solution. A volume of 166 Å$^3$ for one o-difluorobenzene molecule (approximately 21 Å$^3$ for each non-hydrogen atom) is very close to the expected value for C and F atoms. The given formula was corrected for this solvent contribution.

CCDC 1860064 (2) contains the supplementary crystallographic data for this paper. These data can be obtained free of charge via https://summary.ccdc.cam.ac.uk/structure-summary-form (or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44)1223-336-033; or deposit@ccdc.cam.uk).

Table 2: Crystallographic data of 2

<table>
<thead>
<tr>
<th>Property</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Empirical formula</td>
<td>C$<em>{54}$H$</em>{69}$AuClP$_3$·2.75 C$_6$H$_4$F$_2$</td>
</tr>
<tr>
<td>Formula weight</td>
<td>1357.17</td>
</tr>
<tr>
<td>Temperature</td>
<td>130(2) K</td>
</tr>
<tr>
<td>Wavelength</td>
<td>71.073 pm</td>
</tr>
</tbody>
</table>
Crystal system: Monoclinic
Space group: \( P2_1/c \)
Unit cell dimensions:
\[
\begin{align*}
  a &= 1800.76(2) \text{ pm} & \alpha &= 90^\circ \\
  b &= 1336.91(2) \text{ pm} & \beta &= 98.503(1)^\circ \\
  c &= 2686.19(3) \text{ pm} & \gamma &= 90^\circ 
\end{align*}
\]
Volume: 6.3958(1) \( \text{nm}^3 \)
\( Z \): 4
Density (calculated): 1.409 \( \text{Mg/m}^3 \)
Absorption coefficient: 2.474 \( \text{mm}^{-1} \)
\( F(000) \): 2774
Crystal size: 0.35 x 0.15 x 0.10 \( \text{mm}^3 \)
Theta range for data collection: 2.287 to 30.108°
Index ranges:
\[
-25 \leq h \leq 25, -18 \leq k \leq 8, -37 \leq l \leq 37
\]
Reflections collected: 94539
Independent reflections: 17655 \([R(\text{int}) = 0.0563]\)
Completeness to theta = 28.285°: 99.9 %
Absorption correction: Semi-empirical from equivalents
Max. and min. transmission: 1.00000 and 0.93302
Refinement method: Full-matrix least-squares on \( F^2 \)
Data / restraints / parameters: 17655 / 50 / 591
Goodness-of-fit on \( F^2 \): 1.032
Final R indices [\( I > 2\sigma(I) \)]:
\[
R1 = 0.0434, \text{ wR2 = 0.0982}
\]
R indices (all data):
\[
R1 = 0.0697, \text{ wR2 = 0.1075}
\]
Largest diff. peak and hole: 3.362 and -0.912 \( e\cdot\text{Å}^{-3} \)

**TGA/DSC measurements**

The TGA/DSC measurements were performed on a STA 449 F1 Jupiter from NETZSCH, using helium atmosphere and carrier gas. During TGA/DSC, mass fragments could be detected using a QMS 403 C Aeolos from NETZSCH. The samples were prepared in alumina crucibles and a heating rate of 10 K/min was applied.
Fig. 1: TG/DTA of 2 in the temperature range from 35 – 1000 °C with a temperature raise of 10 K/min. Blue – mass of the sample; green – mass flow of 114 g/mol; red – mass flow of 26 g/mol; black – heat of reaction.

References:


