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SUPPORTING INFORMATION

STRUCTURAL EFFECTS OF TRIFLUOROMETHYLATION AND FLUORINATION IN GOLD(I)

BIPHEP FLUOROTHIOLATES

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Experimental Details

Instrumentation and materials

Solvents were dried using established procedures and distilled under nitrogen gas immediately before use¹. Thin layer chromatography (TLC) (Sigma-Aldrich, silica gel 60 F_{254} or neutral aluminium oxide 60 F_{254}) was used to follow the progress of the reactions under examination employiong hexane/ethyl acetate (9:1) as eluent.

Instrumentation: melting points were obtained using a Fisher-Johns apparatus. Infrared spectra were recorded on a Perkin-Elmer FTIR/FIR Spectrum 400 spectrometer in the range of 4000 to 400 cm⁻¹ using Attenuated Total Reflectance (ATR). Elemental analyses were determined utilizing a Thermo Scientific Flash 2000 Analyser at 950 °C. ¹H and ¹³C NMR spectra were registered on a 9.4 T Varian VNMRS spectrometer while ¹⁹F and ³¹P{¹H} NMR were obtained on a 7.0 T Oxford Spectrometer. Chemical shifts are in ppm relative to internal TMS $\delta = 0$ (¹H, ¹³C) and to external references of CFCl₃ (for ¹⁹F) and H₃PO₄ (for ³¹P) at 0 ppm. *J* values are given in Hz. Positive-ion fast atom bombardment mass spectrometer operated at an acceleration voltage of 10 kV. Samples were desorbed from a 3-nitrobenzyl alcohol matrix by 3 keV xenon atoms employing the matrix ions as the reference material.

 $Pb(OOCCH_3)_2$, [KAuCl₄], 2,2'-Bis(diphenylphosphino)biphenyl (BIPHEP) and fluorinated thiols (R_FSH) were purchased from Sigma-Aldrich Co. and used without further purification. Lead thiolates $Pb(SC_6F_5)_2$ and $Pb(SC_6F_4(CF_3)-4)_2$ were prepared by previously reported methods^{2,3}.

Caution: Pb(II) salts are known to be extremely toxic. All procedures were conducted in the fume cupboard.

Synthesis and characterisation

[Au₂Cl₂(μ -BIPHEP)] Similarly to the reported procedure⁴ a mixture of [AuCl(Tetrahidrothiophene)] and BIPHEP in (CH3)2CO/CH2Cl2 (1:1) was stirred

at r.t. for 1.5 h without inert atmosphere. A white material precipitated after addition of hexane in excess.

[Au₂(SC₆F₅)₂(μ-BIPHEP)] a mixture of 59.3 mg (0.060 mmol) of [Au₂Cl₂(μ-BIPHEP)] with 43.4 mg (0.070 mmol) of Pb(SC₆F₅)₂ in 10 mL of acetone was stirred at room temperature for two hours without inert atmosphere. The resulting uncoloured solution volume was reduced to 2 mL and an excess of hexane was added. A white precipitated powder is obtained afterwards. Suitable crystals for structure determination were obtained by slow evaporation of a solution of the compound on a CH₂Cl₂/CH₃CN mixture. Colorless crystalline solid; 73.8% yield; mp: 234-237 °C; elemental analysis found C, 43.80; H, 2.1. Calc. for C₄₈H₂₈Au₂F₁₀P₂S₂: C, 43.85; H, 2.15 %; IR(ATR) ν_{max}(cm⁻¹) 3073.2w, 3006.78w, 1435s, 1078vs(br), 698s; NMR δH (300 MHz; CD₂Cl₂; Me₄Si) 7.80 (4H, m, - C₆H₄H-4), 7.57 – 7.31 (16H, m, -C₆H₄H), 7.13 (2H, m, BIPHEP-5,5'), 6.98 (2H, m, BIPHEP-6,6'), 6.83 (2H, m, BIPHEP-4,4'), 6.15 (2H, m, BIPHEP-3,3').δP{¹H} (121.5 MHz; CD₂Cl₂; H₃PO₄) 28.00 (1 P, s). δF (282.4 MHz; CD₂Cl₂; CFCl₃) -133.8 (2F, m, F_o), -166.8 (1 F, m, F_p), -167.22(2 F, m, F_m). MS-FAB⁺ m/z 1313(M⁺, 2%), 1115 (M-SC₆F₅, 100), 719 (M-Au(SC₆F₅)₂, 20).

[Au₂(SC₆F₄(CF₃)-4)₂(μ-BIPHEP)] a mixture of 65.6 mg (0.066 mmol) of [Au₂Cl₂(μ-BIPHEP)] with 52.7 mg (0.074 mmol) of Pb(SC₆F₄(CF₃)-4)₂ in 10 mL of acetone was stirred at room temperature for two hours without inert atmosphere. The resulting uncoloured solution volume was reduced to 2 mL and an excess of hexane was added. A white precipitated powder is obtained afterwards. Suitable crystals for structure determination were obtained by slow evaporation of a solution of the compound on a CH₂Cl₂/CH₃CN mixture. Colorless crystalline solid; 65.3% yield; mp: 228-230 °C; elemental analysis found C: 42.5, H: 2.1. Calc. for C₅₀H₂₈Au₂F₁₄P₂S₂: C: 42.45, H: 2.0; IR(ATR) v_{max}(cm⁻¹) 3054.8w, 3008.6w, 1479, 1445s, 1091vs, 998.5s, 740s; NMR δH (300 MHz; CD₂Cl₂; Me₄Si) 7.81 (4H, m, -C₆H₄*H*-4), 7.65 – 7.41 (16H, m, -C₆*H*₄H), 7.21 (2H, m, BIPHEP-5,5'), 7.07 (2H, m, BIPHEP-6,6'), 6.92 (2H, m, BIPHEP-4,4'), 6.27 (2H, m, BIPHEP-3,3'). δP{¹H} (121.5 MHz; CD₂Cl₂; H₃PO₄) 62.9 (1 P, s). δF (282.4 MHz; CD₂Cl₂; CFCl₃) -55.54 $(3F, t, {}^{4}J_{F-F} = 21.37 \text{ Hz}, -CF_3), -130.96 (2F, m, F_o), -144.29 (2 F, m, F_m). \text{ MS-FAB}^+$ m/z 1413(M⁺, 2%), 1165 (M-SC₆F₅, 100), 719 (M-Au(SC₆F₅)₂, 40).

X-ray crystallography.

Suitable single crystals of 1 and 2 were mounted on a glass fiber and studied with an Oxford Diffraction Gemini "A" diffractometer with a CCD area detector, with radiation source of $\lambda_{MoK\alpha} = 0.71073$ Å using graphite-monochromatized radiation at 130 K. Unit cell parameters were determined with a set of three runs of 15 frames (1° in ω). The collected data set consisted of 6/503 and 7/508 runs/frames of intensity (1° in ω) for 1 and 2 respectively, and a crystal-to-detector distance of 55.00 mm. The double pass method of scanning was used to exclude any noise. The collected frames were integrated by using an orientation matrix determined from the narrow frame scans. CrysAlisPro and CrysAlis RED software packages were used for data collection and integration^{5,6}. The double pass method of scanning was used to exclude any noise. The collected frames were integrated by using an orientation matrix determined from the narrow frame scans. Final cell constants were determined by a global refinement; collected data were corrected for absorbance by using the analytical numeric absorption correction using a multifaceted crystal model based on expressions upon the Laue symmetry using equivalent reflections⁷. Structure solution and refinement were carried out with the SHELXS-2014 and SHELXL-2014 packages⁸; WinGX v2014.1 software was used to prepare material for publication ^{9,10}. Full-matrix least-squares refinement was carried out by minimizing $(Fo^2 - Fc^2)^2$. All nonhydrogen atoms were refined anisotropically and the refinement was carried out without restraint. Hydrogen atoms attached to carbon atoms were placed in geometrically idealized positions and refined as riding on their parent atoms, with C—H = 095 Å with Uiso (H) = 1.2Ueq(C)for aromatic groups. Structures are available via Crystallographic Data Center as supplementary material number CCDC 1545829- 1545830. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK. E-mail: deposit@ccdc.cam.ac.uk.

Crystal data and experimental details of the structure determination are listed in Table S1.

| Identification code | 1 | 2 |
|--|---|---|
| Empirical formula | $C_{48}H_{28}Au_2F_{10}P_2S_2$ | $C_{50}H_{28}Au_2F_{14}P_2S_2$ |
| Formula weight | 1314.70 | 1414.72 |
| Temperature (K) | 130(2) | 130(2) |
| Wavelength (Å) | 0.71073 | 0.71073 |
| Crystal system | Triclinic | Triclinic |
| Space group | P -1 | P -1 |
| a (Å) | a = 10.9563(5) | a = 10.7502(4) |
| b (Å) | b = 13.2303(6) | b = 13.3823(6) |
| c (Å) | c = 16.1494(7) | c = 17.1566(9) |
| α (°). | $\alpha = 93.295(4)$ | $\alpha = 83.608(4)$ |
| β (°). | $\beta = 101.336(4)$ | $\beta = 77.608(4)$ |
| γ (°). | $\gamma = 110.274(4)$ | $\gamma = 72.188(4)$ |
| Volume (Å ³) | 2132.90(18) | 2292.36(19) |
| Z | 2 | 2 |
| Density (calculated) (Mg/m ³) | 2.047 | 2.050 |
| Absorption coefficient (mm ⁻¹) | 7.123 | 6.648 |
| F(000) | 1252 | 1348 |
| Crystal size (mm ³) | 0.314 x 0.154 x 0.141 | 0.560 x 0.440 x 0.360 |
| Theta range for data collection | 3.390 to 29.599°. | 3.453 to 29.497°. |
| Index ranges | -13<=h<=15, -17<=k<=16, - | -14<=h<=13, -16<=k<=17, - |
| | 22<=l<=22 | 21<=l<=23 |
| Reflections collected | 27978 | 29824 |
| Independent reflections | 10251 [R(int) = 0.0659] | 10901 [R(int) = 0.0737] |
| Completeness to theta = 25.242° | 99.8 % | 99.7 % |
| Refinement method | Full-matrix least-squares on F ² | Full-matrix least-squares on F ² |
| Data / restraints / parameters | 10251 / 0 / 565 | 10901 / 15 / 619 |
| Goodness-of-fit on F^2 | 1.074 | 1.080 |
| Final R indices [I>2 σ (I)] | R1 = 0.0571, wR2 = 0.1425 | R1 = 0.0518, wR2 = 0.1229 |
| R indices (all data) | R1 = 0.0689, wR2 = 0.1566 | R1 = 0.0632, wR2 = 0.1343 |
| Largest diff. peak and hole (e.Å ⁻³) | 5.648 and -3.998 | 3.034 and -4.037 |

Table SI-1. Crystal data and structure refinement for 1 and 2.



Fig S1. ORTEP plot at 50% probability level for compound 1.



Fig S2. ORTEP plot at 50% probability level for compound 2.

Computational Details

Methods

Single point electronic structure calculations at the X-ray experimental geometries were carried out with the BP86 functional^{11,12} along with the Zeroth-Order Regular Approximation (ZORA) ¹³, using the TZV-ZORA basis set¹⁴ to take into account relativistic effects. These calculations were performed with the aid of the ORCA program.¹⁵ This methodology has been successfully exploited to describe metal-metal and metalligand bonding in gold coordination compounds.^{16,17} We used the QTAIM formalism to establish an exhaustive partition of space through the topological analysis of the electron density which allows the recovery of distinct chemical concepts such as bonds, atoms and functional groups.¹⁸ The QTAIM also leads to a rigorous examination of atomic contacts.¹⁹ The use of QTAIM with densities obtained from scalar relativistic-ZORA calculations gives correct descriptions of the molecular electronic structure. ²⁰ All QTAIM computations were carried out with the AIMAII suite of programs.²¹ The NCI index provides a way to study noncovalent interactions by investigating the reduced density gradient (RDG), a quantity of common use in DFT. Peaks in the plot of the relation of the RDG and the electron density evidence different types of non-covalent interactions. A qualitative assessment of the energy associated with these interactions can be derived from plotting the electron density in isosurfaces of the RDG. ²² The NCIPlot program²³ provides useful images for visualising these non-covalent interactions. We utilised the following colour code to represent these interactions: red, blue and green indicate repulsive, attractive, and weak van der Waals interactions respectively as shown in the scale shown in Figure 3. We have exploited this concept to examine the second coordination sphere around the gold centres, and the results have been visualised with the VMD software.²⁴

Structures optimisation

Gas phase geometry optimisations of the molecular structures for compounds 1 and 2 were done with and without the use of the Grimme dispersion correction²⁵. Figure S3 shows the structures optimized including the correction. A comparison of experimental (blue) and optimized with the correction (red) structures is displayed in figure S4. It demonstrates a high degree of similitude. The relevance of the dispersion corrections in the modeling of this kind of weak interactions is exemplified by the structure shown in figure S5 that does not include D3 and which geometry considerably differs from the experimental one.



Fig S3. BP86/Def2-TZVP D3BJ optimized structures for compounds **1** (top) and **2**(bottom) which predict intramolecular contacts are that are closer than those experimentally observed.



Fig S4. Experimental and optimised geometries (BP86/D3BJ) of molecules 1 (top) and 2 (bottom).



Fig S5. Experimental and optimised geometries (BP86) of molecules **1** (top) and **2** (bottom).

Model system study



Fig S6. QTAIM charges of the control systems.

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