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Bidentate amino- and iminophosphine ligands in mono- and dinuclear gold(I) complexes: Synthesis, structures and AuCl displacement by AuC_6F_5

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Abstract

Bidentate imino- and aminophosphine ligands were prepared by firstly a Schiff-base condensation reaction between 2-(diphenylphosphino)benzaldehyde and the corresponding primary amines to afford the imino derivatives and secondly reduction of the imines with $NaBH_4$ to the aminophosphine ligands in satisfactory yields. The ligands readily reacted with chlorogold(I) compounds to produce new mononuclear iminophosphine- and dinuclear aminophosphine chlorogold(I) complexes. Further, reaction of the dinuclear chlorogold complex with $C_6F_5Au(tht)$ (tht = tetrahydrothiophene) led to the displacement of one AuCl moiety by AuC_6F_5 forming a digold(I) mixed halogen/organometallic complex. Both digold(I) complexes displayed intramolecular Au···Au interactions, whilst the di(chlorogold) complex also showed an intermolecular Au··· Au interaction, as determined by X-ray crystallography. The displacement of only one of the two AuCl groups presumably relates to the strength of the Au–P bond (inert) vs. the weakness of the Au–N bond (labile), the latter being more easily broken.

Keywords: Mono- and dinuclear gold(I) complexes; P–N bidentate ligands; Iminophosphine; Aminophosphine; Pentafluorophenyl; X-ray crystal structures

There is a growing interest in the co-ordination chemistry of bi- and multidentate ligands containing both hard (N donor) and soft (P donor) Lewis bases [1,2]. Such hemilabile ligand systems have the potential to bind soft metal centers such as those of the platinum group metals (PGMs) strongly via phosphorus and weakly via nitrogen, which allows for the facile displacement of the chelating N-moiety. This scenario is frequently desired in homogeneous catalytic reactions [3]. The differing reactivity of chelating P–N vs. P–P type ligands has previously been compared [4] and, amongst the PGMs in particular, the catalytic application of P–N-based ligands has been investigated [5,6].

Complexes with bidentate hemilabile ligands show potential not only in catalytic cycles, but also in medicinal applications. For example, various studies of gold(I) have been related to anti-arthritic [7,8], anti-tumour [7,9] and anti-microbial physiological activities [10,11]. Although gold(I) mono- and bisphosphine compounds have been extensively studied [12] together with their mechanisms of cytotoxity and anti-tumour activity [13], bidentate gold(I) compounds that utilise both a hard and soft donor atom are only poorly represented in the literature [14]. Among the 'hard' donor type atoms, the co-ordination chemistry of gold(I) oxygen compounds [15,16] shows a distinct paucity in the literature, while gold(I) complexes with nitrogen donor functions are more common yet less stable than their phosphine analogues [17,18].

We herein report the preparation and characterisation of the three new complexes of gold(I) with bidentate P–N

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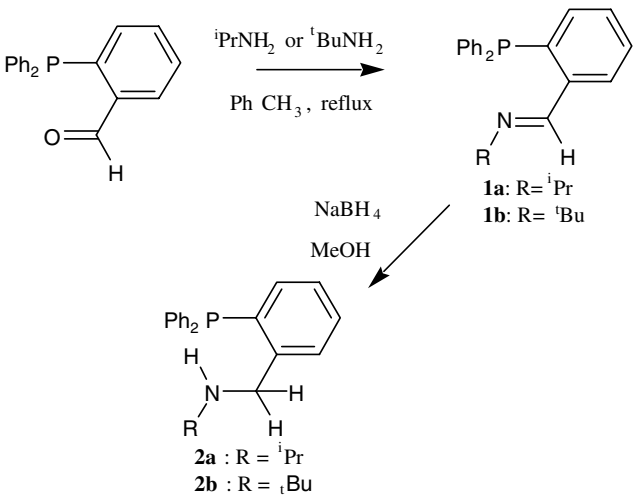
ligands where, depending its nature, the ligand binds to Au(I) either in a mono- or bidentate fashion to form the corresponding Au(I) complexes. Additionally, we report the facile displacement of an N-bound AuCl moiety by an organometallic AuC_6F_5 group.

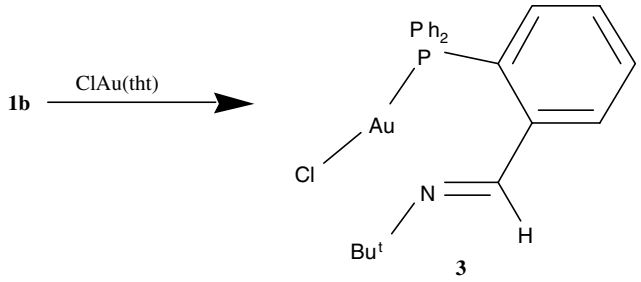
The Schiff-base iminophosphine ligands **1a** and **1b** were prepared using a condensation reaction by treatment of 2-(diphenylphosphino)benzaldehyde with the corresponding primary amines in toluene under reflux and were isolated in high yields (>90%) by vacuum distillation (0.05 mm Hg, 250 °C). Reduction of ligands **1a** and **1b** with $NaBH_4$ in dry MeOH formed analogous amines **2a** and **2b** in satisfactory yields (>70%) after bulb-to-bulb vacuum distillation (0.05 mm Hg, 250 °C). (See Scheme 1).

Complex **3** was prepared [19] by the reaction of iminophosphine ligand **1a** with one or two molar equivalents of ClAu(tht) (tht = tetrahydrothiophene), respectively (Scheme 2). In the case where one equivalent of gold(I) was used, the gold complex was obtained in good yield (73%) in $CHCl_3$ as solvent. However, when two equivalents of the ClAu(tht) were added to the ligand, with the intention of probing the possibility of binding two gold atoms through the P and N atoms, respectively, no dinuclear gold complexes were observed. Instead, autocatalytic decomposition and subsequent reduction of Au(I) to colloidal gold was observed by the presence of an insoluble purple coloured precipitate.

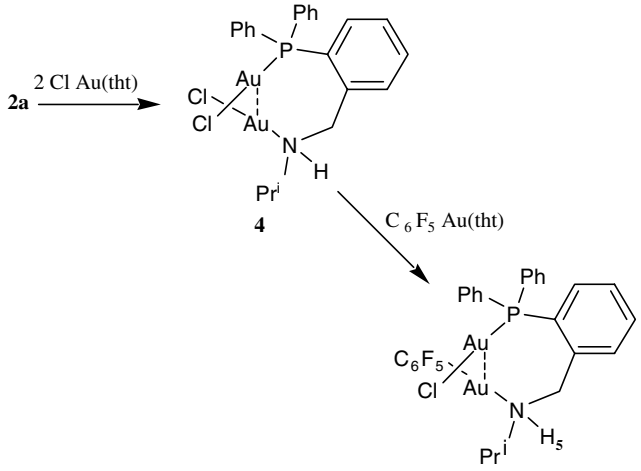
In contrast, when aminophosphine ligand **2a** was reacted with one molar equivalent of ClAu(tht), the reaction proceeded cleanly to produce dinuclear gold(I) complex **4** [20] in 32% yield (Scheme 3). Improvement in the yield to 67% (based on the ligand as a limiting reagent) could be obtained by performing the same reaction using two molar equivalents of the Au(I) reagent. Some decomposition of the Au(I) reagent to Au(0) was also observed in this instance. The formation of both **3** and **4** was complete within 30 minutes as determined by ^{13}P NMR spectroscopy. Here, the free ligands **1b** and **2a** manifested



Scheme 1. Ligand synthesis.



Scheme 2. Preparation of mononuclear gold complex **3**.



Scheme 3. Preparation of dinuclear gold complexes **4** and **5**.

singlet resonances at −11.9 ppm and −15.7 ppm, respectively. Upon complexation, a significant downfield shift of these signals from 31.0 to 26.0 ppm for **3** and **4**, respectively, was observed with concomitant disappearance of the signal of the original free ligand, providing a diagnostic analytical tool by which the complexation process could be followed. In these complexes, the methylene moiety carries two diastereotopic protons (arising from the N-centred chirality induced by Au-complexation). This diastereotopicity is not observed in the NMR spectra of the compounds, possibly due to rapid flexing of the large (by virtue of the two Au atoms contained therein and the relatively long Au–Au bond) seven-membered ring which may preclude a preferred conformation being observable on the NMR time-scale, leading to an averaging of the methylene proton signals to form the observed singlet.

Complex **5** was prepared in a small-scale reaction (Scheme 3) by reaction of chlorogold complex **4** with one molar equivalent of C_6F_5 Au(tht). The reaction led to the selective displacement of the N-bound AuCl fragment in **4** by AuC_6F_5, leaving the already P-bound AuCl moiety intact. To the best of our knowledge, this is the first example of an AuCl fragment being substituted (through N–Au bond cleavage) by an organogold(I) fragment. Since only one of the two AuCl fragments was substituted, the relative P–Au(I) and N–Au(I) bond strengths are contrasted, particularly with regard to the displacement by organometallic

moieties. Displacement of the remaining chlorine atom may be possible through the treatment with LiC_6F_5, which is known [21] to react with chlorogold(I), potentially providing a step-wise synthesis of a bis-organogold(I) compound through selective cleavage of Au–N and Au–Cl bonds.

Single crystals of complexes **3–5** were grown from solution [19,20] and were subjected to X-ray crystallographic analysis [22]. The structure of complex **3** is shown in Fig. 1. The data for **3** did not refine well [22] and the structure is reported primarily for its molecular structure and its comparison with other structures shown: bond lengths and angles for this structure are not used for comparison purposes due to the poor refinement. Nevertheless, no unusual bond angles or distances were observed and the complex showed a virtually linear P–Au–Cl system (bond angle of 177°) as is normally anticipated for two-coordinate Au(I) compounds.

Compared with complex **3**, the most important feature demonstrated by the crystal structures of complexes **4** (Figs. 2 and 3) and **5** (Fig. 4) is that each shows the presence of dinuclear gold(I) centers with Au–Au interactions. The solid state structure of complex **4** is particularly interesting and unusual in that it shows the presence of intramolecular (2.98 Å) as well as intermolecular (3.19 Å) Au···Au interactions (Fig. 3). The intramolecular Au···Au distance is significantly shorter in **4** than it is in **5** (2.98 Å vs. 3.10 Å), presumably as a consequence of the more sterically encumbered aromatic ring in **5** together with electronic factors. In complex **4**, the P–Au–Cl angle (175.26°) is bent slightly further from linearity than that of the lighter N–Au–Cl congener at 177.36°. The crystallography also confirmed the reduction of the imine (shorter imine C=N bond (C37–N1) of 1.25 Å in **3**) to the amine (C–N bond distance (C37–N1) of 1.50 Å in **4**).

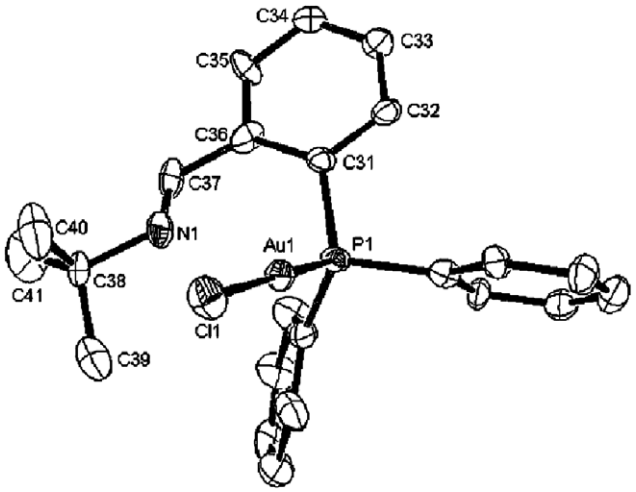


Fig. 1. ORTEP structure of **3** with 50% probability ellipsoids.

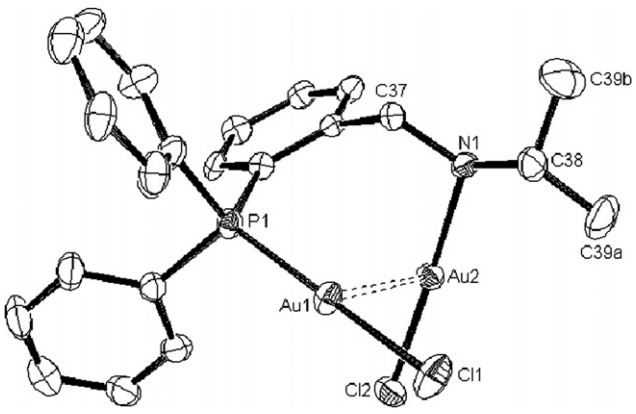


Fig. 2. ORTEP diagram **4** with 50% probability ellipsoids. Selected interatomic distances (Å) and angles (°): C37–N1 1.504(8), C38–C39B 1.479(12), C38–N1 1.507(9), C38–C39A 1.531(11), N1–Au2 2.087(6), Cl1–Au1 2.2916(19), Cl2–Au2 2.2721(18), P1–Au1 2.2380(18), Au1–Au2 2.9821(5) (intra), Au2–Au2 3.1998(6) (inter); N1–C37–C36 110.3(5),C39B–C38–N1 113.0(7), C39B–C38–C39A 111.4(7), N1–C38–C39A 108.2(6),C37–N1–C38 113.4(5), C37–N1–Au2 110.5(4), C38–N1–Au2 114.6(4), P1–Au1–Cl1 175.26(6), P1–Au1–Au2 91.87(4), N1–Au2–Cl2 177.36(15), Cl1–Au1–Au2 92.28(4). (Note: The N-centre is an NH group, not an amide.)

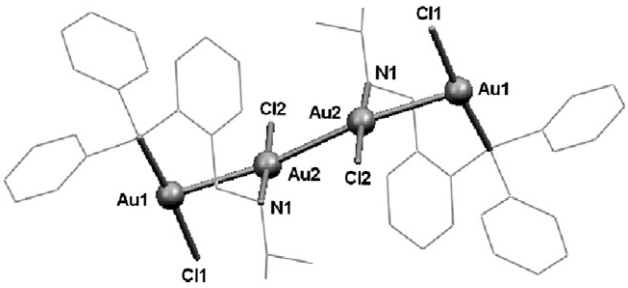


Fig. 3. Portion of the crystal packing for complex **4,** showing intra- and intermolecular gold–gold interactions.

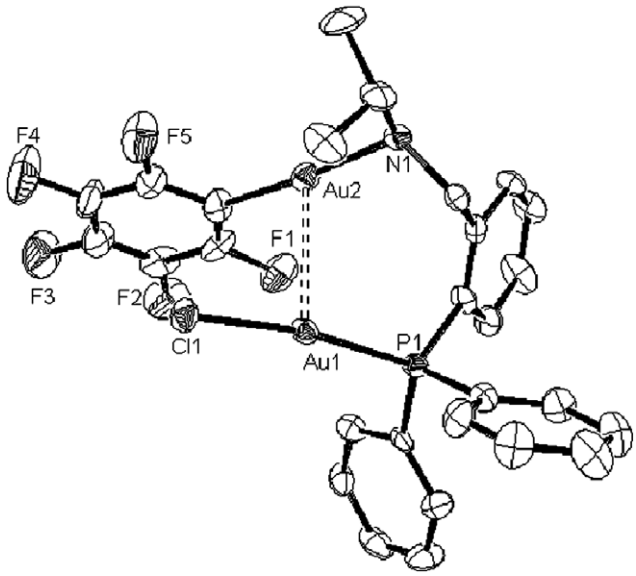


Fig. 4. ORTEP structure of **5** with 50% probability ellipsoids. Selected interatomic distances (Å) and angles (°): N1–Au2 2.110(8), P1–Au1 2.244(2), Cl1–Au1 2.315(2), Au1–Au2 3.1013(10), P1–Au1–Cl1 169.68(8), P1–Au1–Au2 96.39(6). (Note: The N-centre is an NH group, not an amide.)

The solid state structure of the di-gold(I) mixed halogen/organometallic complex **5** is shown in Fig. 4. The P–Au–Cl angle in **5** (169.68°) is significantly more bent than between the same three atoms in complex **4** (175.26°). This may reasonably be attributed to a steric bulk introduced to the system by the additional Au-bound aromatic ring in **5**.

In conclusion, we have demonstrated that P–N bidentate ligands may bind to either one or two Au(I) ions, depending on the system in question. The Au atoms in dinuclear complexes manifested intramolecular Au–Au interactions, as well as intermolecular Au–Au interactions in one instance. We have further shown a rare if not unique Au–Au exchange reaction for this system, replacing inorganic gold(I) for an organogold analogue.

1. Supplementary material

CCDC 624478, 624479 and 624480 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via http://www.ccdc.cam.ac.uk/conts/retrieving.html, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336 033; or e-mail: deposit@ccdc.cam.ac.uk.

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[19] *Synthesis of* **3**: To a stirred solution of **1b** (0.100 g, 0.290 mmol) in diethyl ether (20 mL) was added 1 M equivalent of ClAu(tht) (0.093 g, 0.290 mmol) dissolved in chloroform (5 mL). The mixture was stirred at room temperature for 5 min during which time a precipitate formed. The solvent was decanted and the precipitate washed with diethyl ether (5 × 5 mL) and hexane (3 × 5 mL) and dried in vacuo. Yield (0.125 g, 0.216 mmol) 74%. M.p. 192–194 °C (white powder), 208–210 °C (crystals from layered $CHCl_3$/hexane). ^{1}H NMR (300 MHz, $CDCl_3$): δ_H 8.67 (d, 1H, $J = 1.8$ Hz, imine-H), 7.86 (ddd, 1H, $J = 7.6$, 4.4 and 1.4 Hz, aromatic), 7.61–7.38 (m, 11H, aromatic), 7.31 (tt, 1H, $J = 7.7$ and 1.7 Hz, aromatic), 6.77 (ddd, 1H, $J = 13.2$, 7.8 and 1.2 Hz, aromatic), 0.99 (s, 9H, C(C$\underline{H}_3$)$_3$). ^{13}C NMR (75 MHz, $CDCl_3$)δ_C 153.7 (d, 1C, $J = 6.5$ Hz, imine-C), 139.3 (d, 1C, $J = 7.1$ Hz, C1), 134.3 (d, 4 C, $J = 12.7$ Hz, *ortho*-C phenyl), 134.1 (d, 1C, $J = 7.1$ Hz), 131.7 (d, 1C, $J =$ 2.6 Hz, C5), 131.5 (d, 2C, $J = 2.6$ Hz, *para*-C phenyl), 131.2 (d, 1C, $J = 8.6$ Hz), 130.0 (d, 2C, $J = 63.2$ Hz, *ipso*-C phenyl), 129.7 (d, 1C, $J = 10.5$ Hz), 129.0 (d, 4C, $J = 12.0$ Hz, *meta*-C phenyl), 127.2 (d, 1C, $J = 55.1$ Hz, C2), 58.6 (s, 1C, $\underline{C}$(CH$_3$)$_3$), 29.6 (s, 3C, C(C$\underline{H}_3$)$_3$). ^{31}P NMR (121 MHz, $CDCl_3$) δ_P 31.0 (s, 1P). FAB-MS: m/z 577 $[M + 1]^+$.
[20] *Preparation of* **4**: Similar to **3** but using **2** equivalents of ClAu(tht). White powder. Yield: (0.160 g) 67% yield. M.p. 124–126 °C (powder), 241–243 °C (crystals from $CHCl_3$/hexane). ^{1}H NMR (300 MHz, $CDCl_3$) δ_H 7.65 (m, 1H, aromatic), 7.57–7.42 (m, 11H, aromatic), 7.20 (tt, 1H, $J =$ 7.5 and 1.5 Hz, aromatic), 6.77 (ddd, 1H, $J = 12.9$, 7.8 and 1.2 Hz, aromatic), 4.09 (s, 2H, HNC$\underline{H}_2$R), 2.64 (pentet, 1H, $J = 6.2$ Hz, C$\underline{H}$(CH$_3$)$_2$), 1.30 (broad s, 1H, N$\underline{H}$), 0.84 (d, 6H, $J = 6.3$ Hz, CH(C$\underline{H}_3$)$_2$). ^{13}C NMR (75 MHz, $CDCl_3$) δ_C 144.7 (d, 1C, $J = 11.0$ Hz, C1), 134.4 (d, 4C, $J = 14.0$ Hz, *ortho*-C phenyl), 133.4 (d, 1C, $J = 8.0$ Hz), 131.9 (d, 3C, $J = 2.5$ Hz, *para*-C phenyl, C5), 130.8 (d, 1C, $J = 9.0$ Hz), 129.3 (d, 4C, $J = 12.0$ Hz, *meta*-C phenyl), 129.0 (d, 2C, $J = 62.6$ Hz, *ipso*-C phenyl), 127.2 (d, 1C, $J = 10.0$ Hz), 126.5 (d, 1C, $J = 59.1$ Hz, C2), 50.4 (d, 1C, $J = 11.6$ Hz, HN$\underline{C}$H$_2$), 48.8 (s, 1C, $\underline{C}$H(CH$_3$)$_2$), 22.7 (s, 2C, CH($\underline{C}$H$_3$)$_2$). ^{31}P NMR (121 MHz, $CDCl_3$) δ_P 26.0 (s, 1P). FAB-MS: m/z 566 $[M\text{-}AuCl]^+$. *Preparation of* **5**: To a stirred solution of C_6F_5Au(tht) (0.001 g, 0.0022 mmol) dissolved in dichloromethane (1 mL) was added in a drop-wise manner one molar equivalent of 4 (0.00175 g, 0.0022 mmol) dissolved in dichloromethane (0.5 mL). The mixture was stirred at room temperature for 1 h after which the solvent was evaporated to ca. 0.5 mL. Single crystals suitable for an X-ray analysis could be obtained by the layering of the solution with hexane. Yield (0.00178 g, 0.00192 mmol) 87%. M.p. 168–170 °C (crystals from DCM/hexane). FAB-MS: m/z 894.3 $[M\text{-}Cl]^+$.
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[22] The intensity data were collected at 173 K on a Bruker SMART 1 K CCD diffractometer with area detector using graphite monochromated Mo Kα radiation ($\lambda = 0.71073$ Å, 50 kV, 30 mA). Data

reduction was carried out using the program SAINT+ [23] and face indexed absorption corrections were made using the program XPREP [23]. The structures were solved by direct methods using SHELXTL [24]. Non-hydrogen atoms were first refined isotropically followed by the anisotropic refinement by full matrix least-squares calculations based on F^2 using SHELXTL. Hydrogen atoms were first located in the difference map then positioned geometrically and allowed to ride on their respective parent atoms. Diagrams and publication material were generated using SHELXTL and PLATON [25]. Complex **4** contains a disordered chloroform molecule. Its contribution to the electron density map was accounted for using the PLATON SQUEEZE algorithm. The contribution of the chloroform molecule has been included in the molecular and chemical formulas as well as $F(000)$. Crystal data for **3**:$C_{23}H_{24}AuClNP$; $M = 577.82$ g/mol, monoclinic, space group $P2_1/n$, $a = 11.0466(19)$ Å, $b = 15.638(3)$ Å, $c = 12.6741(19)$ Å, $\beta = 93.709(7)°$, $V = 2184.9(6)$ Å^3, $Z = 4$, $D_c = 1.757$ g cm^{-1}, μ(Mo Kα) = 6.936 mm^{-1}, $F(000) = 1120$, 11936 reflections collected, 5293 unique, $R1 = 0.1180$, $wR2 = 0.2529$ (for all data), $R1 = 0.0889$, $wR2 = 0.2221$, GOF = 1.015. *Crystal data for* **4**:$C_{22}H_{24}Au_2Cl_2NP$ 0.5($CHCl_3$); $M = 857.91$ g/mol, triclinic, space group P-1 (No. 2), $a = 8.1563(10)$ Å, $b = 0.0935(13)$ Å, $c = 16.4581(18)$ Å, $\alpha = 94.575(7)°$, $\beta = 93.152(7)°$, $\gamma = 109.791(7)°$, $V = 1266.0(3)$ Å^3, $Z = 2$, μ(Mo Kα) = 12.019 mm^{-1}, $F(000) = 798$, 16943 reflections measured, 6109 unique, R(int) = 0.084, $R1 = 0.0331$, $wR2 = 0.0988$ (for all data), GOF = 1.087. *Crystal data for* **5**: $C_{28}H_{24}Au_2ClF_5$ NP; $M = 929.84$ g/mol, monoclinic, $P2_1/n$, $a = 8.685(4)$ Å, $b = 14.427(6)$ Å, $c = 22.578(10)$ Å, $\alpha = 90°$, $\beta = 92.900(8)°$, $\gamma = 90°$, $V = 2825(2)$ Å^3, $Z = 4$, $D_c = 2.186$ g cm^{-1}, μ(Mo Kα) = 10.576 mm^{-1}, $F(000) = 1736$, 15880 reflections measured, 6823 unique, R(int) = 0.1067, $R1 = 0.0702$, $wR2 = 0.1481$ (all data), GOF = 1.063.

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