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Synthesis and structures of gold perfluorophthalimido complexes[†]

Nicky Savjani, Simon J. Lancaster, Sean Bew, David L. Hughes and Manfred Bochmann*

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Compounds of the new tetrafluorophthalimido anion, $[C_6F_4(CO)_2N]^-$, are readily accessible by treatment of tetrafluorophthalimide with either LiNPrⁱ₂ or mixtures of NEt₃ and Me₃ECl (E = Si or Sn), to give $C_6F_4(CO)_2N$ -X (X = Li **3**, SiMe₃ **4**, and SnMe₃ **5**). The reaction of the trimethylsilyl derivative **4** with AgF leads cleanly to the ion pair complex $[Ag(NCMe)_2][Ag(N(CO)_2C_6F_4)_2]$ (**6**·2MeCN), which contains a linear $[Ag\{N(CO)_2C_6F_4\}_2]^-$ anion and a tetracoordinate Ag⁺ cation. Compound **6** reacts with iodine to give the N-iodo compound $C_6F_4(CO)_2NI$ **7**, which crystallises as an acetonitrile adduct. Treatment of **6** with LAuCl affords LAu $\{N(CO)_2C_6F_4\}$ (L = Ph₃P **8a**, Cy₃P **8b**, or THT **9**), whereas the reaction with AuCl in acetonitrile affords the heterobinuclear compound $[Ag(MeCN)_2][Au\{N(CO)_2C_6F_4\}_2]$ -MeCN (**10**·3MeCN). The tetrafluorophthalimido ligand is not readily displaced by donor ligands; however, the addition of $B(C_6F_5)_3(Et_2O)$ to a diethyl ether solution of **8a** leads to the salt $[Au(PPh_3)_2][N\{COB(C_6F_5)_3\}_2C_6F_4)]$ **11**. The analogous reaction of (THT)Au $\{N(CO)_2C_6F_4\}$ with $B(C_6F_5)_3$ in toluene in the presence of excess norbornene (nb) gives $[Au(nb)_3][N\{COB(C_6F_5)_3\}_2C_6F_4)]$ **12**. Compounds **11** and **12** contain a new non-coordinating phthalimido-bridged diborate anion with O-bonded boron atoms. The crystal structures of compounds **2–11** are reported.

Introduction

Gold complexes with electron withdrawing π -ligands, particularly perfluorophenyl complexes, show a remarkable and versatile chemistry.¹ As part of our interest in the coordination chemistry of heavy metals with labile ligands,² we decided to explore complexes of the tetrafluorophthalimido anion, $[C_6F_4(CO)_2N]^-$ since this ligand suggested the possibility of extensive charge delocalisation, coupled with the presence of fluorine and C=O moieties as reporter functions for changes in the electronic and bonding characteristics. Gold imidinato complexes have a long history,³ not least because of potential medical applications,⁴ whereas metal complexes of the tetrafluorophthalimido ligand have, to our knowledge, not been described before.

Wolfson Materials and Catalysis Centre, School of Chemistry, University of East Anglia, Norwich, NR4 7TJ, UK. E-mail: m.bochmann@uea.ac.uk; Fax: +44 01603 592044

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Results and discussion

Tetrafluorophthalimide was first synthesised by Gething *et al.* who reacted tetrafluorophthalic acid with an aqueous solution of ammonia, followed by condensation and sublimation, although the yield was low.⁵ A significantly improvement is achieved using a two-step procedure *via* the anhydride **1**, followed by ammonolysis with urea.^{6,7} The product was extracted into hot anisole to give the tetrafluorophthalimide **2** in 71% overall yield (Scheme 1).

Crystals of **2** were grown from slow cooling of an anisole solution and the compound was characterised by X-ray diffraction (Fig. 1). The molecules are planar (C5-C6-N7-H7 torsion angle 179.8°), with extensive conjugation between the nitrogen atom and the C==O moieties. This is reflected in the low Lewis basicity of **2**, *i.e.* its failure to react with a number of strong Lewis acids (AlX₃, BX₃, where X = F, Cl, Br, C₆F₅). In the crystal the molecules form a hydrogen-bonded network in a corkscrew-like arrangement, where the N–H unit of one molecule interacts with one of the two oxygen atoms of a neighbouring molecule (N–H…O 2.07(3) Å).



Scheme 1 Synthesis of tetrafluorophthalimide.



Fig. 1 Crystal packing of 2, with partial labelling scheme; unit cell depicted with the hydrogen bonding shown to illustrate the corkscrew orientation. Selected bond lengths (Å) and angles (°): C(6)-N(7) 1.389(3), N(7)-C(8) 1.380(3), C(6)-O(6) 1.205(3), C(8)-O(8) 1.212(3), N(7)-H(7) 0.80(3), $H(7) \cdots O(8') 2.07(3)$; N(7)-H(7)-O(8') 171(3).

The acidic N–H function of **2** can readily be metallated. Initial attempts to synthesise the lithium phthalimide **3** were unsuccessful; for example, the reaction of n-butyl lithium in THF solution at -78 °C gave a deep red product, the ¹⁹F NMR spectrum of which revealed a large number of broadened peaks. On the other hand, replacing n-butyl lithium with lithium bis(trimethylsilyl)amide under the same conditions generated the trimethylsilyl phthalimide **4** in moderate yield (~40%) (Scheme 2). The lithium phthalimide is however accessible in good yield



Scheme 2 Preparation of metallated perfluorophthalimido compounds.

from **2** and lithium diisopropylamide in diethyl ether as a red, amorphous solid. Attempts to obtain crystals failed. The compound contained variable amounts of diethyl ether and a satisfactory elemental analysis could therefore not be obtained; however, the ¹⁹F NMR and infrared spectroscopic data confirmed the presence of the phthalimido anion. In particular, the v(C==O) stretching frequency is reduced from 1740 cm⁻¹ in **2** to 1640 cm⁻¹ in **3**.

The trimethylsilyl derivative 4 is more conveniently prepared by treating 2 with triethylamine and excess trimethylsilyl chloride. An analogous procedure using Me_3SnCl affords the trimethylstannyl derivative 5.

Crystals of **4** could be grown by cooling a light petroleum solution, while those of **5** were grown from diethyl ether. The molecular structures of **4** and **5** are shown in Fig. 2 and 3, respectively. Both unit cells contain two independent but nearidentical molecules but with very different packing arrangements: whereas the silyl compound shows approximately parallel but alternating stacking of the tetrafluorophthalimido groups, the tin analogue does not.

The *N*-silyl derivative **4** is a useful phthalimide anion equivalent. Thus the reaction of **4** with AgF in acetonitrile at room temperature gives the argentate salt Ag[Ag{N(CO)₂C₆F₄}₂] **6** in almost quantitative yield. While the solvent of crystallisation is readily lost under vacuum, recrystallisation of this complex from acetonitrile layered with diethyl ether gives the adduct [(MeCN)₂Ag][Ag{N(CO)₂C₆F₄}₂] as pale-brown crystals



Fig. 2 Molecular structures of two independent molecules of 4 (left) and its packing in the crystal (right), illustrating differences in packing within the unit cell. Selected bond lengths (Å):4: Molecule 1: C(2)-N(1) 1.405(7), N(1)-C(9) 1.402(7), C(2)-O(2) 1.207(6), C(9)-O(9) 1.212(6), N(1)-Si(1) 1.821(5). Molecule 2: C(12)-N(11) 1.391(8), N(11)-C(19) 1.400(8), C(12)-O(12) 1.220(8), C(19)-O(19) 1.190(7), N(11)-Si(2) 1.831(5).



Fig. 3 Molecular structures of two independent molecules of 5, showing the atomic numbering scheme. Selected bond lengths (Å): Molecule 1: C(2)-N(1) 1.390(3), N(1)-C(9) 1.383(3), C(2)-O(2) 1.208(3), C(9)-O(9) 1.217(3), N(1)-Sn(1) 2.183(2). Molecule 2: C(12)-N(11) 1.401(3), N(11)-C(19) 1.378(3), C(12)-O(12) 1.208(3), C(19)-O(19) 1.215(3), N(11)-Sn(11) 2.156(2).

(Scheme 3). The same product can be obtained using the tin reagent 5 (91% yield); however, removal of the Me₃SnF by-product is less convenient.

The crystal structure of 6.2MeCN (Fig. 4) reveals that the compound contains two different silver environments: a linear bis(phthalimido)argentate(I) anion which coordinates in chelate fashion to an $[Ag(MeCN)_2]^+$ cation *via* two of the carbonyl moieties.⁸ The geometry of the latter is a strongly flattened tetrahedron, with wide O–Ag–O and N–Ag–N angles in the range of 137–142° and consequently more acute N–Ag–O angles. The two planes of the phthalimido ligands are parallel to one another.

The distance between the two silver atoms is 3.0172(3) Å, well above the sum of the covalent radius for Ag(1) in the anion in **6** (1.33 Å) and the ionic radius of tetracoordinate Ag⁺ (1.15 Å). The structure is reminiscent of the succinimidate [Ag(H₂O)][Ag(suc)₂], which shows similar Ag–N distances of 2.079(5) and 2.067(5) Å but also coordination of the Ag⁺ ion to an O-atom of a neighbouring succinimidate.⁹

Whereas the reactions of the Si and Sn compounds 4 and 5 with Cl_2 and Br_2 under mild conditions gave only the parent phthalimide 2 as the only isolable product, while there was no reaction with iodine, the reaction of the silver salt 6 with iodine



Scheme 3 Preparation and reactions of silver and gold perfluorophthalimido complexes.



Fig. 4 Molecular structure of $[(MeCN)_2Ag][Ag\{N(CO)_2C_6F_4\}_2]$ (6·2MeCN) showing the atom numbering scheme. Selected bond lengths (Å) and angles (°): Ag(1)–N(1) 2.055(2), Ag(1)–N(11) 2.074(2), Ag(2)–O(9) 2.4616(17), Ag(2)–O(12) 2.4885(17), Ag(2)–N(31) 2.219(2), Ag(2)–N(41) 2.238(2), N(1)–C(9) 1.362(3), N(1)–C(2) 1.381(3); N(1)–Ag(1)–N(11) 174.16(8), O(9)–Ag(2)–O(12) 137.18(6), N(31)–Ag(2)–N(41) 142.45(9), O(9)–Ag(2)–N(41) 83.31(8), O(9)–Ag(2)–N(31) 112.53(7), O(12)–Ag(2)–N(41) 95.91(8), O(12)–Ag(2)–N(31) 93.95(7).

in dry dioxane under the exclusion of light produced the N-iodo compound $C_6F_4(CO)_2NI$ 7 as a yellow powder in good yield (82%) (Scheme 3). The v(CO) frequency was observed at 1702 cm⁻¹, slightly lower than in 2 (1740 cm⁻¹). Recrystallisation of 7 from acetonitrile at -28 °C gave crystals of the adduct 7·MeCN (Fig. 5). The whole of the phthalimide molecule lies on a mirror-plane of symmetry. Only the nitrogen atom of the MeCN solvent refined slightly away from the same plane. While the formation of an acetonitrile adduct indicates a positively polarised iodine atom,

the iodine-nitrogen distance of 2.601(19) Å is substantially longer than the iodine-nitrogen distances in cationic iodine complexes (*cf.* $[I(NCMe)_2]^+$, 2.198(3) Å).¹⁰

The molecular planes of 7 are separated by 3.152 Å (half the *b* cell length), but the phthalimide molecules overlap only peripherally with closest contact $C(7) \cdots C(7')$ at 3.173(2) Å. The phthalimide and the MeCN molecules are aligned with $N(1)-I(1) \cdots N(11)-C(12)$ almost linear, with a short $I(1) \cdots N(11)$ interaction.



Fig. 5 Molecular structure of $C_6F_4(CO)_2NI$ ·MeCN 7·MeCN, showing the atom numbering scheme. Selected bond lengths (Å) and angles (°): $N(1)-C(2) 1.405(17), N(1)-C(9) 1.391(14), C(2)-O(2) 1.184(14), C(9)-O(9) 1.214(15), I(1)-N(1) 2.074(9), N(11)-C(12) 1.15(3), I(1) \cdots N(11) 2.601(19); C(2)-N(1)-I(1) 121.2(7), C(9)-N(1)-I(1) 125.5(8), C(9)-N(1)-C(2) 113.4(9), O(2)-C(2)-N(1) 124.7(11), N(1)-I(1) \cdots N(11) 174.6(3), C(12)-N(11)-I(1) 168.5(10).$



Fig. 6 The two independent molecules of **8a** showing a partial atomic numbering scheme (left) and side view of the stacking arrangement (right) in which molecules are stacked in groups of four almost parallel ring systems about a centre of symmetry. Selected bond lengths (Å) and angles (°): Au(1)-P(1) 2.2370(11), Au(1)-N(41) 2.058(4), Au(2)-P(6) 2.2336(12), Au(2)-N(91) 2.042(4); N(41)-Au(1)-P(1) 171.19(11), N(91)-Au(2)-P(6) 173.90(11).

Although, in view of the electron withdrawing character of the $C_6F_4(CO)_2N$ moiety, compound 7 could be expected to readily undergo oxidative addition reactions, *e.g.* with gold(I) phosphine complexes, no such reactions were observed, and the starting materials were recovered.

The reaction of AuCl(PPh₃) with either the silver salt **6** or lithium phthalimide **3** in acetonitrile at room temperature gives (triphenylphosphine)gold tetrafluorophthalimide **8a** as colourless crystals in good yields (77 and 74% respectively). This complex is stable to air and moisture. The carbonyl stretch is observed at 1678 cm⁻¹, indicative of the accumulation of partial negative charge on the N-ligand. The tricyclohexylphosphine analogue **8b** was prepared similarly. A number of related succinimidato and heterocyclic gold(1) phosphine complexes are known.^{11,12} Crystals of both products were grown from toluene.

The molecular structures of **8a** and **8b** are shown in Fig. 6 and 7, respectively. Both have the expected linear gold coordination geometry. The unit cell of **8a** contains two independent molecules.

The essentially coplanar phthalimido ligands are arranged at an angle of about 90° (Fig. 6), such that a C=O moiety of one ligand is positioned on top of the six-ring of the second. Complex **8b** crystallises with a (disordered) molecule of toluene (Fig. 7). Molecules are stacked in columns: pairs of phthalimide ligands are parallel about a centre of symmetry, with close contacts between overlapping edges, *e.g.* $C(14) \cdots F(14')$ 3.185, $N(11) \cdots C(14')$ 3.226, $C(12) \cdots C(14')$ 3.264, $C(12) \cdots C(13')$ 3.270 and $C(13) \cdots C(13')$ 3.272 Å. On the opposite faces, there are the disordered toluene molecules, tilted at 17.3(4)° to the phthalimide planes, with close contacts of $F(14) \cdots C(53)$ 3.183, $C(14) \cdots C(52)$ 3.304 and $C(13) \cdots C(52)$ 3.567 Å.

The bond lengths show remarkably little variation with the nature of the phosphine ligands, with **8b** showing a slightly longer Au–P and slightly shorter Au–N distance than **8a**. However, both compare well with related non-fluorinated complexes, notably $(Et_3P)Au\{N(CO)_2C_6H_4\}$ (Au–P 2.238(6), Au–N 2.05(2) Å)¹³ and with (Ph₃P)Au{N(CO)_2C_6H_4} (Au–N 2.028(4) and 2.040(4) Å).¹⁴



Fig. 7 Molecular structure of $(Cy_3P)Au\{N(CO)_2C_6F_4\}$ toluene **8b**, showing the atomic numbering scheme. Selected bond lengths (Å) and angles (°): Au–P(2) 2.2476(9), Au–N(11) 2.052(3); N(11)–Au–P(2) 172.54(9).

These Au–N bond lengths are longer than typical gold amide bonds, *e.g.* in (Ph₃P)AuN(SiMe₃)₂ (2.027 Å),¹⁵; they are however about 0.05 Å shorter than the Au–N distance in (Ph₃P)Au(NTf₂) (Au–P 2.231, Au–N 2.102 Å),¹⁶ a good indication that anionic charge delocalisation in phthalimides and perfluorophthalimides is much less effective than in the N(SO₂CF₃)₂ anion. In line with this observation, the complexes **8a** and **8b** do not react with diphenylacetylene, bis(trimethylsilyl)acetylene, cyclooctyne, norbornene, methyl acrylate, CO, trimethylsilylcyanide, *t*butylcyanide or excess tricyclohexylphosphine.

In an attempt to generate phthalimido complexes with more labile donor ligands, the tetrahydrothiophene complex $(THT)Au\{N(CO)_2C_6F_4\}$ 9 was prepared by a similar route. The compound is stable to air and moisture but light sensitive, giving the colourless crystals a purple hue after exposure for a day. The molecular structure is shown in Fig. 8. The compound crystallises with one molecule of toluene. While the N–Au–S moiety has the expected linear geometry, the packing arrangement in the crystal is rather different from that in **8a** and **8b** and shows minimal overlap between the phthalimide ligands of two neighbouring molecules. Instead, the Au atoms are arranged to form a chain based on Au ··· Au interactions. The Au–N distance in 9-toluene is notably

shorter than in the phosphine analogues; evidently the weaker donor strength of the sulfur ligand is replaced by tighter anion binding and aurophilic interactions.

Attempts to generate perfluorophthalimido complexes of the LAuX type with even weaker ligands L, such as acetonitrile, were only partially successful. Although the reaction of **6** with AuCl in a 1:1 stoichiometric ratio in acetonitrile gave a pale yellow solution which contained a single phthalimido complex (by ¹⁹F NMR spectroscopy), the attempted isolation and crystallisation led to decomposition and formation of a gold film. On the other hand, the reaction of AuCl with two equivalents of **6** yielded the mixed-metal complex Ag[Au{N(CO)₂C₆F₄}₂] **10** as a brown powder. Crystals of this compound were grown by the slow cooling of a hot acetonitrile solution. This affords the adduct [(MeCN)₂Ag][Au{N(CO)₂C₆F₄}₂]·MeCN (**10**·3MeCN). The structure (Fig. 9) resembles that of **6**·2MeCN, except that the phthalimido ligands have been transferred to gold.

The bis(phthalimido)aurate anion is linear. The Au–N distances in **10** are *ca.* 0.03–0.05 Å shorter than in the neutral complexes **8** and **9**. We are aware of only one crystallographically characterised precedent for a structure of this type, sodium bis(1methylhydantoinato)gold·4H₂O, for which a slightly shorter Au–N bond length of 1.94 Å has been reported.^{4b}

Unlike in 6, the phthalimido ligands in 10 are twisted with respect to one another, with a dihedral angle of 14.8° . The aurate anion binds to a silver cation *via* two of the carbonyl oxygen atoms, but with two distinctly different Ag...O distances, unlike the near-symmetrical chelate found in 6.2MeCN. The Ag...O coordination is reflected in the infrared spectrum which shows two C=O stretching bands at 1653 and 1620 cm⁻¹ for the non-coordinated and the silver-bound C=O moieties, respectively. The non-bonding distance of the two metal centres is 2.9544(2) Å.

While there was no evidence of lability of gold-bound phthalimide or its displacement by excess phosphine, the ligand is easily removed from the coordination sphere on addition of $B(C_6F_5)_3$. Thus, treating **8a** with $B(C_6F_3)_3(Et_2O)$ in diethyl ether at room temperature for 15 min generates $[Au(PPh_3)_2][N\{COB(C_6F_5)_3\}_2C_6F_4]$ **11**, which contains a perfluorophthalimido-bridged diborate anion. The borane molecules are bonded to the O atoms; there is no evidence for formation of an N-bonded borate. The B–O bonding is reflected in the v(CO) frequencies which change from 1678 cm⁻¹ for **8a** to 1545 cm⁻¹ in **11**. Crystals of **11** were grown from a minimum amount of toluene layered with light petroleum at -30 °C and obtained as pale yellow platelets. The structure of **11** (Fig. 10) shows a linear [Au(PPh_3)_2]⁺ cation supported by the bulky phthalimidodiborate anion; there are no close cation-anion interactions.

Since the starting material has a P: Au ratio of 1:1, attempts were made to use this reaction for the preparation of mixed-ligand gold complexes of the type $[(R_3P)AuL']^+$ in the presence of L' = norbornene or 1,5-cyclooctadiene (PR₃ = PPh₃ or PCy₃). There was no evidence for the formation of such compounds. However, the reaction of the more labile tetrahydrothiophene complex **9** with B(C₆F₅)₃ in toluene in the presence of excess norbornene at 0 °C resulted in the displacement of the sulfur ligand and formation of $[Au(nb)_3][{N(COB(C_6F_5)_3)_2C_6F_4]$ **12.** Crystals were grown from dichloromethane at -30 °C. The $[Au(nb)_3]^+$ cation has recently been reported as the SbF₆⁻ salt;^{17,18}



Fig. 8 Molecular structure (top) and packing arrangement of 9-toluene. Selected bond lengths (Å) and angles (°): Au–S(1) 2.264(4), Au–N(11) 2.025(12), Au–Au' 3.3218(3); N(11)–Au–S(1) 179.5(3); Au'-Au–Au'' 172.58(4).

Comparison of spectroscopic characteristics of the tetrafluorophthalimido ligand

The tetrafluorophthalimido ligand allows the fluorine atoms and C=O functions to be used as probes for the electronic characteristics. A comparison of these data is given in Table 1. The C=O stretching frequencies show the expected reduction with increasing anionic character of the ligand but are little influenced by the donor strength of ligands coordinated to gold, *e.g.* the values for the PPh₃, PCy₃ and THT complexes are identical. The ionic O-chelate **10** shows two C–O bands, the higher of which is reduced by 87 cm⁻¹ compared to the parent phthalimide **2**, while the second shows a further reduction by 33 cm⁻¹ due as a result of coordination to Ag⁺. There is however a more substantial reduction in C– O bond order on borane coordination; *e.g.* the corresponding absorption for compound **11** is almost over 190 cm⁻¹ lower than v(CO) in **2**.

By comparison, given the wide ¹⁹F chemical shift range, the variations of the ¹⁹F signals for this set of complexes are quite small; in fact the chemical shift are more strongly influenced

Table 1 Comparison of IR and ${}^{19}\mathrm{F}\ NMR$ data (in CDCl_3)

			¹⁹ F NMR			
Compound	IR $v_{\rm C=0}/{\rm cm}^{-1}$	Solvent	Signal 1	Signal 2	Δδ	
2	1740	CDCl ₃	-134.7	-141.2	6.5	
2	1740	CD ₃ CN	-139.9	-146.0	6.5	
3	1640	$THF-d_8$	-143.7	-152.5	8.8	
4	1706	CDCl ₃	-137.0	-142.7	5.7	
5	1706	CDCl ₃	-137.9	-144.2	6.3	
6	1587	CD ₃ CN	-143.6	-150.7	7.1	
7	1702	CD_3CN	-139.4	-146.5	7.1	
8a	1678	CDCl ₃	-139.2	-145.9	6.7	
8b	1679	CDCl ₃	-139.7	-146.4	6.7	
9	1678	CDCl ₃	-138.8	-145.9	7.1	
10	1653, 1620	CD ₃ CN	-143.0	-149.7	6.7	
11	1545	CDCl ₃	-133.5	-141.0	7.5	
12	n.d.	CDCl ₃	-132.1	-141.3	9.2	

by the solvent than by any negative charge or donor ligands in the complex. In spite of the presence of F substituents, there is evidently very limited charge delocalisation over the C_6F_4 part of the phthalimido ligand.



Fig. 9 Molecular structure of $[(MeCN)_2Ag][Au\{N(CO)_2C_6F_4)\}_2]$ -MeCN (10·3MeCN), showing the atomic numbering scheme. Selected bond lengths (Å) and angles (°):Au–N(1) 1.9972(17), Au–N(11) 2.0030(17), Ag–O(2) 2.4358(16), Ag–O(19) 2.6598(15), Ag–N(21) 2.207(2), Ag–N(31) 2.194(2). N(1)–Au–N(11) 177.73(7), N(21)–Ag–N(31) 130.95(8), O(2)–Ag–O(19) 140.68(5).



Fig. 10 Crystal structure of $[Au(PPh_3)_2][\{N(COB(C_6F_5)_3)_2C_6F_4\}]$ 11, showing a partial atomic numbering scheme. Selected bond lengths (Å) and angles (°): Au–P(1) 2.297(5), Au–P(2) 2.301(5), B(3)–O(32) 1.57(2), B(9)–O(39) 1.55(3), N(31)–C(32) 1.31(2), N(31)–C(39) 1.31(2), C(32)–O(32) 1.23(2), C(32)–C(33) 1.48(2), C(33)–C(38) 1.37(2); P(1)–Au–P(2) 169.53(19), B(3)–O(32)–C(32) 128.0(14), O(32)–C(32)–N(31) 131.8(17), N(31)–C(39)–O(39) 131.0(17), C(39)–O(39)–B(9) 127.1(14), C(32)–N(31)–C(39) 113.3(15).

Tetrafluorophthalimido ligands readily form complexes with Li, Si, Sn, I, Ag and Au. The Si and Sn derivatives are useful phthalimide anion equivalents. While gold complexes of the type LAu(phthalimide) have ample structural precedents, in the absence of donor ligands the less common linear $[M(phthalimide)_2]^-$ are formed (M = Ag or Au) which form heterobimetallic structures with Ag⁺ ions. The Au-N bonds in phosphine gold complexes $LAu\{N(CO)_2C_6F_4\}$ are only very slightly longer than those in non-fluorinated analogues, which points to a surprisingly small influence of the C₆F₄ ring on the bonding character of this ligand. In line with this, there was no displacement of the $[N(CO)_2C_6F_4]$ ion by excess phosphines. On the other hand, the addition of the strongly Lewis acidic borane $B(C_6F_5)_3$ led to facile phthalimide abstraction and the formation of a new non-coordinating diborate anion. This method can be used for the generation of gold complexes with weak donor ligands such as olefins.

Experimental

All manipulations were performed under dry nitrogen, using standard Schlenk techniques. Nitrogen was purified by passing through columns of supported P_2O_5 , with moisture indicator, and activated 4 Å molecular sieves. Solvents were pre-dried over sodium wire (toluene, light petroleum, THF, diethyl ether) or calcium hydride (dichloromethane), and distilled under argon over sodium (toluene), sodium-potassium alloy (light petroleum, bp 40–60 °C), sodium-benzophenone (THF, diethyl ether) or calcium hydride (dichloromethane). LiNPri₂,¹⁹ LiN(SiMe₃)₂,²⁰ (Ph₃P)AuCl²¹ were prepared following literature methods. Deuterated solvents were stored over activated 4 Å molecular sieves and degassed by several freeze-thaw cycles.

Infrared spectra were obtained using a Perkin Elmer Spectrum BX FT-IR spectrometer equipped with a diamond ATR attachment. ¹H, ¹³C{¹H}, ¹¹B and ¹⁹F NMR spectra were recorded using a Bruker DPX300 spectrometer. ¹H NMR spectra (300.13 MHz) were referenced to the residual protons of the deuterated solvent used. ¹³C NMR spectra (75.47 MHz) were referenced internally to the D-coupled ¹³C resonances of the NMR solvent. ¹¹B (96.3 MHz) and ¹⁹F (282.4 MHz) NMR spectra were referenced externally to BF₃·Et₂O or CFCl₃, respectively. Elemental analyses were performed by London Metropolitan University.

Synthesis of tetrafluorophthalimide (2)

The synthesis was adapted from literature procedures.^{6,7} A 250 mL three-necked flask with a reflux condenser and an addition funnel was charged with 2,3,4,5-tetrafluorophthalic acid (25.1 g, 105.4 mmol). Thionyl chloride (40 mL) was added dropwise over 15 min at 60 °C. The subsequent white suspension was heated to 90 °C overnight to afford a light-brown solution. The excess thionyl chloride was removed *in vacuo* and the resulting ivory solid dried under vacuum. The crude tetrafluorophthalic anhydride 1 (22.1 g, 95.9 mmol, 91%) was used without further purification. The analytical data for this compound were in agreement with the literature data.⁶

For the conversion into the phthalimide, a mixture of 1 (5.70 g, 25.9 mmol) and urea (1.63 g, 27.2 mmol) was heated at 135 $^{\circ}$ C

for 10 min, upon which the contents melted and then re-solidified. The crude phthalimide was dissolved in the minimum amount of hot anisole (40 mL), filtered and recrystallised at 2 °C to produce yellow crystals of **2** (4.42 g, 20.2 mmol, 78%). ¹⁹F NMR (CDCl₃, 282.4 MHz): δ –134.7 (2F, dd, $J_{\text{F-F}}$ = 19.8, 8.5 Hz, *F2*, *F5*), -141.2 (2F, dd, $J_{\text{F-F}}$ = 19.8, 8.5 Hz, *F3*, *F4*). ¹⁹F NMR (CD₃CN, 282.4 MHz): δ –139.9 (2F, dd, $J_{\text{F-F}}$ = 19.8, 8.5 Hz, *F2*, *F5*), -146.0 (2F, dd, $J_{\text{F-F}}$ = 19.8, 8.5 Hz, *F3*, *F4*). IR: 1740 cm⁻¹ v(C=O).

Lithium tetrafluorophthalimide (3)

To a solution of **2** (1.05 g, 4.8 mmol) in diethyl ether (20 mL) was added a solution of LiNPrⁱ₂ (0.512 g, 4.8 mmol) in diethyl in -78 °C. The mixture was stirred for 1 h to give an orange solution which was allowed to warm to room temperature. Removal of the solvent left **3** as an orange solid. The attempted recrystallisation by dissolving this solid in diethyl ether (20 mL) and layering with toluene at 2 °C resulted in the precipitation of a powder (740 mg, 3.3 mmol, 69%). ¹⁹F NMR (THF-*d*₈, 282.4 MHz): δ –143.7 (2F, br. s, *F2*, *F5*), –152.5 (2F, br. s, *F3*, *F4*). IR (nujol mull) 1640 cm⁻¹ v(C=O).

N-Trimethylsilyltetrafluorophthalimide (4)

In a 1 L round bottom flask, 2 (13.6 g, 62 mmol) was dissolved in 300 mL dry THF and cooled to -80 °C. To this was added trimethylchlorosilane (15.7 mL, 124 mmol) followed by dry triethylamine (8.7 mL, 62 mmol). A white precipitate formed. The reaction was warmed to 20 °C and stirred for 1h. The solvent was removed in vacuo, the residue dissolved in light petroleum and recrystallised at 2 °C to yield yellow needles. The crystals were filtered off and washed with cold petroleum to produce 4 as pale yellow needles (8.1 g, 28 mmol, 45%). ¹H NMR (CDCl₃, 300 MHz): δ 0.48 (9H, s, Me). ¹⁹F NMR (CDCl₃, 282.4 MHz): δ -137.0 (2F, dd, $J_{\text{F-F}}$ = 19.8, 8.5 Hz, F2, F5), -142.7 (2F, dd, $J_{\text{F-F}} = 19.8, 8.5 \text{ Hz}, F3, F4$). ¹³C{¹H} NMR (CDCl₃, 75.5 MHz): δ -0.51 (s, Me), 115.81 (s, *ipso*-C), 142.4 (dm, $J_{C-F} = 271$ Hz, Ar-C), 144.3 (dm, $J_{C-F} = 278$ Hz, Ar-C), 166.5 (s, C=O). IR (powder) 1706 cm⁻¹ v(C=O). Anal. found: C, 45.41 H, 3.00; N, 4.91%. Calcd for C₁₁H₉F₄NO₂Si: C, 45.36; H, 3.11; N, 4.81.

N-Trimethylstannyltetrafluorophthalimide (5)

The compound was made following the procedure described for **4**, with the exception that the product was recrystallised from diethyl ether at 2 °C to. Yellow crystals of **5** were obtained (5.65 g, 14.9 mmol, 67%). ¹H NMR (CDCl₃, 300.1 MHz): δ 0.72 (9H, s, Me). ¹⁹F NMR (CDCl₃, 282.4 MHz) δ –137.9 (2F, dd, *J*_{F-F} = 19.8, 8.5 Hz, *F2*, *F5*), –144.2 (2F, dd, *J*_{F-F} = 19.8, 8.5 Hz, *F3*, *F4*). ¹³C{¹H} NMR (CDCl₃, 75.5 MHz): δ –3.71 (s, Me), 116.4 (s, *ipso*-C), 142.6 (dm, *J*_{C-F} = 263 Hz, *Ar*-C), 144.6 (dm, *J*_{C-F} = 274 Hz, *Ar*-C), 169.0 (s, C=O). IR (powder): 1706 cm⁻¹ v(C=O). Anal. Found: C, 34.71; H, 2.45; N, 3.70. Calcd for C₁₁H₉F₄NO₂Sn: C, 34.60; H, 2.38; N, 3.67%.

Disilver bis(tetrafluorophthalimide) (6)

In a 250 mL round bottom flask, the silyl derivative **4** (4.40 g, 15.1 mol) was dissolved in 70 mL dry acetonitrile and silver fluoride (1.92 g, 15.1 mmol) was added. The mixture was stirred at room

temperature for 30 min to yield a hazy solution. The solvent was removed *in vacuo*. The straw coloured solid residue was redissolved in dry acetonitrile (20 mL). Addition of diethyl ether (50 mL) yielded a fluffy straw-coloured solid which was filtered off, washed with diethyl ether and dried to give **6** (4.51 g 6.9 mmol, 92%). The compound can be obtained free of coordinating solvent by prolonged evacuation. ¹⁹F NMR (CD₃CN, 282.4 MHz): δ –143.6 (4F, m, *F2*, *F2'*, *F5*, *F5'*), –150.7 (4F, m, *F3*, *F3'*, *F4*, *F4'*). ¹³C{¹H} NMR (CD₃CN, 75.5 MHz): δ 119.1 (s, *ipso*-C), 141.3 (dm, *J*_{C-F} = 263 Hz, *Ar*-C), 143.3 (dm, *J*_{C-F} = 261 Hz, *Ar*-C), 173.9 (s, C==O). IR (powder): 1587 cm⁻¹ v(C==O). Anal. Found: C, 29.33; N, 4.32. Calcd for C₁₆Ag₂F₈N₂O₄: C, 29.48; N, 4.30%. For single crystal X-ray analysis, the product was recrystallised from acetonitrile layered with diethyl ether, to give pale straw coloured needles of **6**·2MeCN.

N-Iodo(tetrafluoro)phthalimide (7)

To a solution of iodine (0.76 g, 3.00 mmol) in dry 1,4-dioxane (10 mL) was added **6** (1.00 g, 3.06 mmol). The reaction was stirred in the dark for 10 min. After removal of the solvent under vacuum at 40 °C, the residue was taken up in acetonitrile, the silver iodide filtered off and the orange filtrate concentrated *in vacuo* to give the *N*-iodo compound **7** as a yellow solid (0.84 g, 2.43 mmol, 82%). ¹⁹F NMR (CD₃CN, 282.4 MHz): δ –139.4 (2F, dd, J_{F-F} = 19.8, 8.5 Hz, *F2*, *F5*), –146.5 (2F, dd, J_{F-F} = 19.8, 8.5 Hz, *F3*, *F4*). IR (nujol mull): 1702 cm⁻¹ v(C=O). Anal. Found: C, 27.89; N, 4.17. Calcd for C₈F₄INO₂: C, 27.85; N, 4.06%. Crystallisation from acetonitrile gave crystals of **7**·MeCN.

Synthesis of $(Ph_3P)Au\{N(CO)_2C_6F_4\}$ (8a)

To a solution of 6 (0.502 g, 1.55 mmol) in dry acetonitrile (50 mL) was added (triphenylphosphine)gold(I) chloride (0.768 g, 1.55 mmol). The reaction was stirred at room temperature for 30 min. The resulting mixture was filtered through celite to give a clear yellow-green solution. The solvent was removed and the residue recrystallized from the minimum amount of toluene, to yield 8a as colourless crystals (0.790 g, 1.19 mmol, 77%). The crystals were suitable for single crystal X-ray analysis. ¹H NMR (CDCl₃, 300.1 MHz): δ 7.5 (m, Ph). ¹⁹F NMR (CDCl₃, 282.4 MHz) δ -139.2 (2F, dd, $J_{F-F} = 22.6$, 5.6 Hz, F2, F5), -145.9 (2F, dd, $J_{F-F} =$ 22.6, 5.6 Hz, F3, F4). ¹³C{¹H} NMR (CDCl₃, 75.5 MHz): δ 117.8 (s, ipso-C), 129.4 (s, Ph), 132.1 (s, Ph), 134.2 (s, Ph), 142.0 (dm, $J_{C-F} = 262$ Hz, Ar-C), 144.2 (dm, $J_{C-F} = 267$ Hz, Ar-C), 172.2 (s, C==O). ³¹P NMR (CDCl₃, 121.5 MHz): δ 32.3 (s). IR (powder): 1678 cm⁻¹ v(C=O). Anal. Found: C, 46.13; H, 2.30; N, 2.10. Calcd for C₂₆H₁₅AuF₄NO₂P: C, 46.10; H, 2.23; N, 2.07%.

Synthesis of $(Cy_3P)Au\{N(CO)_2C_6F_4\}$ (8b)

Using the procedure described for **8a**, the reaction yielded **8b** as colourless crystals (0.646 g, 0.82 mmol, 74%). The crystals grown were suitable for single crystal X-ray analysis. ¹H NMR (CDCl₃, 300.1 MHz): δ 1.23 (6H, br, m), 1.42 (12H, br, m), 1.70 (3H, br, m), 1.85 (6H, br, m), 2.04 (6H, br, m). ¹⁹F NMR (CDCl₃, 282.4 MHz) δ –139.7 (2F, dd, J_{F-F} = 19.8, 5.6 Hz, *F2*, *F5*), –146.4 (2F, dd, J_{F-F} = 19.8, 5.6 Hz, *F3*, *F4*). ¹³C{¹H} NMR (CDCl₃, 75.5 MHz): δ 21.8–35.9 (8 signals, Cy), 141.8 (dm, J_{C-F} = 258 Hz, *Ar*-C), 143.9 (dm, J_{C-F} = 266 Hz, *Ar*-C), 172.5 (s, C==O). ³¹P NMR (CDCl₃,

121.5 MHz): δ 50.9 (s). IR (powder): 1679 cm⁻¹ v(C=O). Anal. Found: C, 50.25; H, 5.18; N, 1.71. Calcd for C₃₃H₄₁AuF₄NO₂P: C, 50.32; H, 5.25; N, 1.78%.

Synthesis of $(C_4H_8S)Au\{N(CO)_2C_6F_4\}$ (9)

Using the procedure described for **8a**, **9** was obtained from (THT)AuCl as pale yellow crystals (283 mg, 0.56 mmol, 56%). The crystals grown were suitable for single crystal X-ray analysis. ¹H NMR (CDCl₃, 300.1 MHz): δ 2.21 (4H, br. s), 3.42 (4H, br. s). ¹⁹F NMR (CDCl₃, 282.4 MHz) δ –138.8, (2F, dd, J_{F-F} = 19.8, 8.5 Hz, *F2*, *F5*), –145.9 (2F, dd, J_{F-F} = 19.8, 8.5 Hz, *F3*, *F4*). ¹³C{¹H} NMR (CDCl₃, 75.5 MHz): δ 30.4 (s, *THT*), 39.8 (s, *THT*), 120.2 (s, *ipso*.C), 141.7 (dm, J_{C-F} = 266 Hz, *Ar*-C), 144.4 (dm, J_{C-F} = 271 Hz, *Ar*-C), 170.9 (s, C=O). IR (powder): 1678 cm⁻¹ v(C=O). Anal. Found: C, 28.74; H, 1.66; N, 2.85. Calcd for C₂₆H₁₅AuF₄PO₂N: C, 28.64; H, 1.60; N, 2.78%.

Synthesis of Silver bis(tetrafluorophthalimido)aurate(I) (10)

To a solution of 6 (0.810 g, 1.24 mmol) in acetonitrile (20 mL) was added AuCl (142 mg, 0.61 mmol). The mixture was stirred for 30 min. The resulting mixture was filtered through celite to give a pale-brown solution. The solvent was removed and the residue was dried. The reaction yielded 10 as a dark brown powder (282.4 mg, 0.38 mmol, 63%). ¹⁹F NMR (CD₃CN, 282.4 MHz) δ-143.0 (4F, dd, $J_{F-F} = 17.0$, 5.7 Hz, F2, F2', F5, F5'), -149.7 (4F, dd, $J_{F-F} =$ 17.0, 5.7 Hz F3, F3', F4, F4'). ¹³C{¹H} NMR (CD₃CN, 75.5 MHz): δ 141.9 (dm, J_{C-F} = 256 Hz, Ar-C), 143.8 (dm, J_{C-F} = 266 Hz, Ar-C), 171.7 (s, C=O). Further analysis was carried out after removing the solvent molecules in a vacuum; IR (powder): 1653 and 1620 cm⁻¹ v(C=O). Anal. Found: C, 26.01; N, 3.70. Calcd for C₁₆F₈AgAuN₂O₄: C, 25.93; N, 3.78%. For single crystal Xray analysis, a hot concentrated acetonitrile solution was allowed to cool slowly, resulting in the formation of brown crystals of $[(MeCN)_2Ag][Au\{N(CO)_2C_6F_4\}_2] \cdot MeCN (10 \cdot 3MeCN).$

Attempted synthesis of (tetrafluorophthalimido)gold(I)·acetonitrile

The procedure described for **10** was used, except that a 1:1 stoichiometric ratio of **6** and AuCl was used. A pale yellow acetonitrile solution resulted. ¹⁹F NMR (CDCl₃, 282.4 MHz) δ –141.3, (2F, dd, $J_{F-F} = 19.8, 8.5$ Hz, *F2*, *F5*), –145.9 (2F, dd, $J_{F-F} = 19.8, 8.5$ Hz, *F3*, *F4*). IR (MeCN solution): 1676 cm⁻¹ v(C=O). Concentration of this solution and attempts to isolate the product resulted in decomposition to metallic gold.

Synthesis of $[(Ph_3P)_2Au][N(COB(C_6F_5)_3)_2C_6F_4]$ (11)

To a solution of **8a** (204 mg, 0.30 mmol) and triphenylphosphine (77 mg, 0.30 mmol) in dry diethyl ether (30 mL) was added at room temperature B(C₆F₅)₃·Et₂O (346 mg, 0.60 mmol). The mixture was stirred for 15 min, the solvent was removed and the yellow solid residue recrystallised from a minimum amount of toluene layered with light petroleum. Yellow crystals of **11** were obtained (452 mg, 0.23 mmol, 78%), suitable for single crystal X-ray analysis. ¹H NMR (CDCl₃, 300.1 MHz): δ 7.48 (30H, m, Ph). ¹⁹F NMR (CDCl₃, 282.4 MHz) δ –115.9 (12F, t, *J*_{F-F} = 22.4 Hz, *o*-*F* C₆F₅), –133.5 (2F, br. s, *F2*, *F5*), –141.0 (2F, br. s, *F3*, *F4*), –158.2 (6F, t, *J*_{F-F} = 22.4 Hz *p*-*F* C₆F₅), –162.3 (12F, m, *m*-*F* C₆F₅). ³¹P NMR

Compound	2	4	5	6-2MeCN	7.MeCN
Empirical formula	$C_8HF_4NO_2$	$C_{11}H_9F_4NO_2Si$	$C_{11}H_9F_4NO_2Sn$	$\begin{array}{c} C_{20}Ag_2F_8N_2O_4 \cdot \\ C_4H_6N_2 \end{array}$	$C_8F_4INO_2{\cdot}C_2H_3N$
Formula weight	219.1	291.3	381.9	734.0	386.0
Crystal system	Monoclinic	Monoclinic	Monoclinic	Monoclinic	Monoclinic
Space group	$P2_1/c$ (no. 14)	$P2_1/c$ (no. 14)	$P2_1/c$ (no. 14)	$P2_1/c$ (no. 14)	$P2_1/m$ (no. 11)
a/Å	12.0520(5)	9.5135(8)	19.1926(6)	7.93961(12)	9.4073(7)
b/Å	5.4998(2)	24.759(2)	6.6264(2)	26.9636(4)	6.3030(5)
c/Å	11.4291(4)	10.7793(6)	20.1512(7)	10.48883(15)	10.1518(10)
$\alpha/^{\circ}$	90	90	90	90	90
$\beta/^{\circ}$	94.626(4)	91.391(6)	90.257(3)	105.245(2)	108.929(9)
$\gamma/^{\circ}$	90	90	90	90	90
Volume/Å ³	755.09(5)	2538.3(3)	2562.76(14)	2166.43(5)	569.39
No. of formula units, Z	4	8	8	4	2
Calculated density/Mg m ⁻³	1.927	1.524	1.980	2.250	2.252
F(000)	432	1184	1472	1408	364
Absorption coefficient μ/mm^{-1}	0.203	0.231	2.039	1.915	2.865
Crystal colour, shape	very pale yellow flat prism	colourless plate	colourless block	colourless plate	colourless hexagonal plate
Crystal size/mm	$0.60 \times 0.30 \times 0.06$	$0.30 \times 0.24 \times 0.06$	$0.22 \times 0.10 \times 0.06$	$0.47 \times 0.24 \times 0.12$	$0.18 \times 0.18 \times 0.01$
θ range/°	3.4 to 25.0	3.1 to 20.0	3.4 to 30.0	3.3 to 27.5	3.6 to 25.0
Limiting indices	$-14 \le h \le 14, -6 \le k \le 6.$	$-9 \le h \le 9, -23 \le k \le$	$-27 \le h \le 27, -9 \le k$	$-10 \le h \le 10, -35 \le k$	$-11 \le h \le 11, -7 \le k \le$
e	$-13 \le l \le 13$	$23, -10 \le l \le 10$	$\leq 9, -28 \leq l \leq 28$	$\leq 35, -13 \leq l \leq 13$	$7, -12 \le l \le 12$
Max. and min. transmission	1.069 and 0.926	1.029 and 0.967	1.112 and 0.873	1.038 and 0.978	1.054 and 0.962
Reflections collected (not including absences)	13776	27063	48849	47568	6985
No. of unique reflections, R_{int}	1334, 0.075	2357, 0.203	7468, 0.070	4974, 0.044	1103, 0.104
No. of 'observed' reflections $(I > I)$	1181	1262	5577	4481	902
$2\sigma_{I}$)					
Data/restraints/parameters	1334/0/140	2357/0/343	7468/0/349	4974/0/367	1103/0/119
Goodness-of-fit on F^2	1.129	0.869	0.912	1.181	1.063
Final <i>R</i> indices ('observed' data)	$R_1 = 0.044, wR_2 = 0.097$	$R_1 = 0.052, wR_2 = 0.039$	$R_1 = 0.029, wR_2 = 0.056$	$R_1 = 0.025, wR_2 = 0.050$	$R_1 = 0.057, wR_2 = 0.116$
Final <i>R</i> indices (all data)	$R_1 = 0.056, wR_2 = 0.103$	$R_1 = 0.145, WR_2 = 0.049$	$R_1 = 0.050, wR_2 = 0.058$	$R_1 = 0.031, wR_2 = 0.051$	$R_1 = 0.079, wR_2 = 0.123$
Largest diff. peak and hole/e $\rm \AA^{-3}$	0.24 and -0.23	0.20 and -0.19	0.82 and -0.80	0.65 and -0.53	2.45 and -1.04

Table 2	Crystal and	structure refinement	data for comp	ounds 2, 4,	5, 6 and 7
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(CDCl₃, 121.5 MHz) 30.1 (s). ¹¹B NMR (CDCl₃, 96.3 MHz): δ –2.7 (br). IR (nujol mull): 1545 cm⁻¹ v(C==O).

Synthesis of $[Au(nb)_3][N(COB(C_6F_5)_3)_2C_6F_4]$ (12)

To a mixture of **9** (50 mg, 0.10 mmol) and norbornene (94 mg, 1.00 mmol) in dry toluene (10 mL) cooled to 0 °C was added tris(pentafluorophenyl)borane (130 mg, 0.25 mmol). The reaction was left to stir at 0 °C for 1 h. The resulting solution was filtered and the solvent was removed *in vacuo* to leave a yellow solid. Recrystallisation in the minimum amount of dichloromethane at -30 °C gave **12** as yellow crystals in moderate yield (92 mg, 0.05 mmol, 54%). The crystals were suitable for X-ray analysis. ¹H NMR (CDCl₃, 300.1 MHz): δ 0.94 (2H, d, $J_{\text{H-H}} = 9.7$ Hz), 1.01 (2H, d, $J_{\text{H-H}} = 10.2$ Hz), 1.23 (2H, dd, $J_{\text{H-H}} = 8.5$, 2.0 Hz), 1.74 (2H, d, $J_{\text{H-H}} = 8.5$ Hz), 3.02 (2H, s), 5.72 ppm (2H, s). ¹⁹F NMR (CDCl₃ 282.4 MHz): δ -114.2 (12F, t, $J_{\text{F-F}} = 19.6$ Hz, o-F C₆F₅), -132.1 (2F, dd, $J_{\text{F-F}} = 19.7$, 8.4 Hz, F2, F5), -141.3 (2F, dd, $J_{\text{F-F}} = 19.7$, 8.4 Hz, F2, 6, 5, -106 Hz, *m*-F C₆F₅), -165.4 (12F, m, *p*-F C₆F₅). ¹¹B NMR (CDCl₃, 96.3 MHz): δ 1.9 (br).

X-Ray Crystallography

Crystals of compounds 2, 4, 5, 6·2MeCN, 7·MeCN, 8a, 8b, 9·toluene and 10·3MeCN were examined at 140(1) K on an Oxford Diffraction Xcalibur-3/Sapphire3-CCD diffractometer, equipped with Mo-K α radiation and graphite monochromator; compound

11 was measured at 120(2) K on a Bruker-Nonius KappaCCD diffractometer (at the EPSRC National Crystallography Service). Intensity data were measured by thin-slice ω - and φ -scans. Crystal data and experimental details are collated in Table 2 and Table 3.

Data were processed using the CrysAlisPro-CCD and -RED²² programs, or for **11**, the DENZO/SCALEPACK²³ programs. The structures were determined by the direct methods routines in the SHELXS program²⁴ and refined by full-matrix least-squares methods, on F²'s, in SHELXL²⁴ In general, the non-hydrogen atoms were refined with anisotropic thermal parameters, although some atoms of disordered groups in compounds **9** and **11** did not refine satisfactorily and were later treated isotropically. Hydrogen atoms were included in idealised positions and their U_{iso} values were set to ride on the U_{eq} values of the parent carbon atoms. Refinement results are included in Table 2. Scattering factors for neutral atoms were taken from reference 25. Computer programs used in this analysis have been noted above, and were run through WinGX²⁶ on a Dell Precision 370 PC at the University of East Anglia.

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Compound	8a	8b .0.5 toluene	9.toluene	10.3MeCN	11
Empirical formula	$C_{26}H_{15}AuF_4NO_2P$	$C_{26}H_{33}AuF_4NO_2P \cdot 0.5(C_7H_8)$	$\mathrm{C_{12}H_8AuF_4NO_2S}\ \mathrm{C_7H_8}$	$C_{20}H_6AgAuF_8N_4O_4$ CH_2CN	$C_{80}H_{30}AuB_2F_{34}NO_2.$ ca 1.5 (C ₄ H ₈ O)
Formula weight	677.3	741.5	595.3	864.2	2071.73
Crystal system	Monoclinic	Triclinic	Monoclinic	Triclinic	Monoclinic
Space group	$P2_1/c$ (no. 14)	$P\overline{1}(no. 2)$	$P2_1/c$ (no. 14)	<i>P</i> 1(no. 2)	$P2_1/n$ (no. 14)
a/Å	13.79281(11)	11.3527(8)	11.8670(17)	8.24928(9)	15.4133(11)
b/Å	12.00838(11)	11.7282(9)	23.7634(14)	9.49150(15)	32.505(2)
c/Å	28.1090(3)	11.9341 (9)	6.6297(5)	16.8812(3)	16.4236(12)
$\alpha/^{\circ}$	90	74.895(6)	90	94.1577(13)	90
$\beta/^{\circ}$	100.4139(10)	69.615(7)	90.071(9)	94.4125(11)	89.997(2)
$\gamma/^{\circ}$	90	72.833(6)	90	111.3597(12)	90
Volume/Å ³	4578.99(7)	1400.86(18)	1869.6(3)	1220.12(3)	8228.3(10)
No. of formula units, Z	8	2	4	2	4
Calculated density/Mg m ⁻³	1.965	1.758	2.115	2.352	1.672
F(000)	2592	734	1136	812	4072
Absorption coefficient μ/mm^{-1}	6.553	5.363	8.034	6.911	1.956
Crystal colour, shape	colourless plate	colourless block, cut from prism	colourless rod	colourless block	pale-yellow block
Crystal size/mm	$0.41 \times 0.38 \times 0.08$	$0.16 \times 0.15 \times 0.14$	$0.50 \times 0.04 \times 0.03$	$0.28 \times 0.18 \times 0.16$	$0.14 \times 0.09 \times 0.05$
θ range/°	3.3 to 30.0	3.4 to 30.0	3.4 to 22.5	3.4 to 30.0	2.9 to 22.5
Limiting indices	$-19 \le h \le 19, -16 \le k$	$-15 \le h \le 15, -16 \le$	$-12 \le h \le 12, -25 \le k \le$	$-11 \le h \le 11, -13 \le k$	$-16 \le h \le 16, -34 \le k$
e	$\leq 16, -39 \leq l \leq 39$	$k \le 16, -16 \le l \le 16$	$25, -7 \le l \le 7$	$\leq 13, -23 \leq l \leq 23$	$\leq 35, -17 \leq l \leq 17$
Max. and min. transmission	1.325 and 0.497	1.159 and 0.796	1.177 and 0.827	1.278 and 0.676	1.000 and 0.651
Reflections collected (not including absences)	117169	15566	18667	34701	37322
No. of unique reflections, R_{int}	13315, 0.071	8119, 0.043	2437, 0.119	7115, 0.041	10292, 0.075
No. of 'observed' reflections $(I > 2\sigma_1)$	11064	7071	1759	6535	8628
Data/restraints/parameters	13315/0/631	8119/0/362	2437/0/219	7115/12/390	10292/0/1145
Goodness-of-fit on F^2	1.214	1.051	1.043	1.042	1.036
Final <i>R</i> indices ('observed' data)	$R_1 = 0.052, wR_2 = 0.070$	$R_1 = 0.031, wR_2 = 0.079$	$R_1 = 0.052, wR_2 = 0.091$	$R_1 = 0.017, wR_2 = 0.041$	$R_1 = 0.088, wR_2 = 0.179$
Final <i>R</i> indices (all data)	$R_1 = 0.072, wR_2 = 0.074$	$R_1 = 0.038, wR_2 = 0.083$	$R_1 = 0.082, wR_2 = 0.099$	$R_1 = 0.021, wR_2 = 0.042$	$R_1 = 0.111, wR_2 = 0.1924$
Largest diff. peak and hole/e $Å^{-3}$	1.80 and -2.43	2.79 and -3.68	1.59 and -1.09	0.86 and -0.91	1.95 and -1.34

Table 3 Crystal and structure refinement data for compounds 8a, 8b, 9, 10 and 11

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