

Synthesis and interconversions of digold(I), tetragold(I), digold(II), gold(I)-gold(III) and digold(III) complexes of fluorine-substituted aryl carbanions.

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Table S1. Analytical data for gold complexes of 2-C₆F₄PPh₂ and C₆H₃-*n*-F-2-PPh₂ (*n* = 5, 6).^a

Compound	C	H	P	F	X
[Au ₂ (μ-2-C ₆ F ₄ PPh ₂) ₂] 2	40.58(40.78)	2.05(1.90)	5.69(5.84)		
[Au ₂ (μ-C ₆ H ₃ -5-F-2-PPh ₂) ₂] 3	45.28(45.40)	2.78(2.75)		3.57(3.99)	
[Au ₂ (μ-C ₆ H ₃ -6-F-2-PPh ₂) ₂] 4	44.93(45.40)	2.81(2.75)	6.45(6.50)	3.74(3.99)	
[Au ₂ X ₂ (μ-2-C ₆ F ₄ PPh ₂) ₂] 5	38.23(38.22)	2.06(1.78)	5.67(5.48)		
[Au ₂ X ₂ (μ-C ₆ H ₃ -5-F-2-PPh ₂) ₂] 6	43.07(42.25)	3.07(2.56)		3.22(3.71)	6.67(6.93)
[Au ₂ X ₂ (μ-C ₆ H ₃ -6-F-2-PPh ₂) ₂] 7	43.79(42.25)	2.92(2.56)		3.18(3.71)	7.11(6.93)
[Au ₂ X ₂ (μ-2-C ₆ F ₄ PPh ₂) ₂] 8	35.30(35.44)	1.68(1.65)	5.01(5.08)		
[Au ₂ X ₂ (μ-C ₆ H ₃ -5-F-2-PPh ₂) ₂] 9	39.48(38.87)	2.57(2.36)		3.52(3.42)	13.46(14.37)
[Au ₂ X ₂ (μ-C ₆ H ₃ -6-F-2-PPh ₂) ₂] 10	39.59(38.87)	2.66(2.36)		3.41(3.42)	14.10(14.37)
[Au ₂ X ₂ (μ-C ₆ H ₃ -5-F-2-PPh ₂) ₂] 12	36.14(35.85)	2.27(2.17)		2.91(3.15)	21.11(21.04)
[Au ₂ X ₂ (μ-C ₆ H ₃ -6-F-2-PPh ₂) ₂] 13	36.25(35.85)	2.56(2.17)		2.90(3.15)	21.25(21.04)
[Au ₂ (OAc) ₂ (μ-2-C ₆ F ₄ PPh ₂) ₂] 14	42.51(40.77)	2.90(2.22)	5.31(5.26)		
[Au ₂ (ONO ₂) ₂ (μ-2-C ₆ F ₄ PPh ₂) ₂] 15	36.71(35.61)	1.86(1.70)	4.94(5.23)		2.34(2.37)
[Au ₂ (OBz) ₂ (μ-2-C ₆ F ₄ PPh ₂) ₂] 16	46.42(46.10)	3.00(2.32)	4.71(4.76)		
[Au ^{II} ₂ (O ₂ CCF ₃) ₂ (μ-2-C ₆ F ₄ PPh ₂) ₂] 17	37.64(37.35)	1.73(1.57)	4.77(4.82)		
[Au ^{II} ₂ (C ₆ F ₅) ₂ (μ-2-C ₆ F ₄ PPh ₂) ₂] 18	41.58(41.43)	1.49(1.45)		24.89(24.52)	
[Au ₂ ^{I,III} (CH ₃) ₂ (μ-2-C ₆ F ₄ PPh ₂) ₂] 19	41.93(41.85)	2.40(2.40)			
[Au ₄ (μ-2-C ₆ F ₄ PPh ₂) ₄] 21	39.88(40.78)	1.96(1.90)	5.67(5.84)	14.65(14.33)	
[XAu(μ-2-C ₆ F ₄ PPh ₂)(κ ² -2-C ₆ F ₄ PPh ₂)AuX] 25	38.23(38.22)	1.92(1.78)	5.71(5.48)		
[XAu(μ-2-C ₆ F ₄ PPh ₂)(κ ² -2-C ₆ F ₄ PPh ₂)AuX] 26	35.99(35.44)	2.16(1.65)			
[XAu(μ-2-C ₆ F ₄ PPh ₂)(κ ² -2-C ₆ F ₄ PPh ₂)AuX] 27	33.13(32.90)	1.83(1.53)			
[XAu(μ-2-C ₆ H ₃ -6-F-2-PPh ₂)(κ ² -C ₆ H ₃ -6-F-2-PPh ₂)AuX] 28	42.13(42.25)	2.77(2.56)	5.81(6.05)	3.37(3.71)	6.58(6.93)
[Au ₂ X ₂ (2,2'-Ph ₂ P-5-F-C ₆ H ₃ C ₆ H ₃ -5-F-PPh ₂)] 32	41.92(42.25)	2.67(2.56)		4.04(3.71)	6.57(6.93)
[Au ₂ X ₂ (2,2'-Ph ₂ P-5-F-C ₆ H ₃ C ₆ H ₃ -5-F-PPh ₂)] 33	38.35(38.87)	2.52(2.36)		3.88(3.42)	
[Au ₂ X ₂ (2,2'-Ph ₂ P-5-F-C ₆ H ₃ C ₆ H ₃ -5-F-PPh ₂)] 34	35.67(38.85)	2.27(2.17)		2.85(3.15)	
[BzOAU(μ-2-C ₆ F ₄ PPh ₂)(κ ² -2-C ₆ F ₄ PPh ₂)AuOBz] 37	46.49(46.10)	2.71(2.32)	4.47(4.76)	11.25(11.67)	
[Au ₂ X ₄ (μ-2-C ₆ F ₄ PPh ₂) ₂] 39	35.47(35.97)	1.91(1.68)	5.43(5.15)	12.28(12.64)	
[Au ₂ X ₄ (μ-2-C ₆ F ₄ PPh ₂) ₂] 40	29.22(31.33)	1.53(1.46)	4.25(4.49)	10.24(11.01)	
[X ₃ Au(μ-2-C ₆ F ₄ PPh ₂)(κ ² -2-C ₆ F ₄ PPh ₂)AuX] 41	35.60(35.97)	1.73(1.68)			11.91(11.80)
[X ₃ Au(μ-2-C ₆ F ₄ PPh ₂)(κ ² -2-C ₆ F ₄ PPh ₂)AuX] 42	31.83(31.33)	1.45(1.46)			

^a Calculated values (%) in parentheses. X = Cl in **6**, **7**, **28**, **32** and **41**; Br in **9** and **10**; I in **12**; N in **15**.

Table S2. Crystal data and details of data collection and structure refinement for complexes 2 (monoclinic

Compound	2	5	8	25
Formula	[Au ₂ (μ-2-C ₆ F ₄ PPh ₂) ₂]	2[Au ₂ Cl ₂ (μ-2-C ₆ F ₄ PPh ₂) ₂].2.5(CH ₂ Cl ₂)	2[Au ₂ Br ₂ (μ-2-C ₆ F ₄ PPh ₂) ₂].2.5(CH ₂ Cl ₂)	[ClAu(μ-2-C ₆ F ₄ PPh ₂)(κ ² -2-C ₆ F ₄ PPh ₂)AuCl].CH ₂ Cl ₂
fw	1067.91	2474.98	2655.36	1216.26
Crystal system	Monoclinic	Monoclinic	Monoclinic	Orthorhombic
Space group	P2 ₁ /n	P2 ₁ /c	P2 ₁ /c	P2 ₁ 2 ₁ 2 ₁
a, Å	12.7411(5)	17.2172(1)	17.4374(1)	10.1958(1)
b, Å	12.9877(6)	21.7718(2)	21.6957(2)	16.5651(2)
c, Å	19.6902(8)	22.8310(2)	22.8416(2)	22.7112(3)
β, deg	99.839(2)	111.2521(5)	109.8587(5)	90
V, Å ³	3210.4(2)	7976.18(11)	8127.48(12)	3835.80 (8)
Z	4	4	4	4
Cryst dimens (mm)	0.34 × 0.31 × 0.22	0.30 × 0.09 × 0.08	0.40 × 0.18 × 0.08	0.40 × 0.10 × 0.08
D _{calc} (Mg m ⁻³)	2.209	2.061	2.170	2.106
μ (mm ⁻¹)	9.475	7.796	9.488	8.070
T, K	200	200	200	200
No. indep rflns (R _{int})	7378 (0.077)	18243 (0.086)	18591 (0.052)	8801 (0.042)
No. obsd rflns [I > 3σ(I)]	4549	8879	10971	7309
No. params refined	441	992	992	507
R _F	0.0429	0.0246	0.0229	0.0261
R _w	0.0458	0.0287	0.0269	0.0302
P _{max} /P _{min} (e Å ⁻³)	1.5/-2.92	1.10/-1.15	1.16/-1.04	5.22/-2.05

and triclinic forms), 4-8, 11, 15-19, 21-22, 24,25, 28, 32, 33, 35, 36, 41 and 42.

Compound	2	4	6
Formula	[Au ₂ (μ-2-C ₆ F ₄ PPh ₂) ₂]	[Au ₂ (μ-C ₆ H ₃ -6-F-2-PPh ₂) ₂]	[Au ₂ Cl ₂ (μ-C ₆ H ₃ -5-F-2-PPh ₂) ₂]
fw	1060.39	952.44	1122.07
Crystal system	Triclinic	Triclinic	Monoclinic
Space group	P-1	P-1	P2 ₁ /c
a, Å	10.7539(2)	9.0115(2)	16.6877(2)
b, Å	12.7320(2)	9.5208(2)	20.0851(3)
c, Å	12.8969(2)	10.0842(2)	11.64580(10)
α, deg	90.4600(10)	89.7260(10)	90
β, deg	113.9920(10)	78.8100(10)	95.7130(10)
γ, deg	98.3480(10)	63.1070(10)	90
V, Å ³	1591.77(5)	753.54	3883.98(8)
Z	2	1	4
D _{calc} (Mg m ⁻³)	2.212	2.099	1.919
μ (mm ⁻¹)	9.381	9.867	7.846
T, K	110(2)	100(2)	100(2)
Cryst dimens (mm)	0.11 × 0.06 × 0.06	0.22 × 0.20 × 0.10	0.34 × 0.30 × 0.17
Theta range, deg	2.78-28.00	2.60-40.00	2.65-33.00
Reflections collected	53442	33955	80609
unique (R _{int})	7679(0.0644)	9335 (0.0637)	14619 (0.0834)
Data / Restraints / Parameters	7679 / 0 / 433	9335 / 0 / 191	14619 / 42 / 466
Final R indices [I > 2σ(I)]	R1 = 0.0240, wR2 = 0.0537	R1 = 0.0271, wR2 = 0.0650	R1 = 0.0402, wR2 = 0.1046
R indices (all data)	R1 = 0.0470, wR2 = 0.0591	R1 = 0.0315, wR2 = 0.0663	R1 = 0.0542, wR2 = 0.1100
Largest diff. peak and hole (e.Å ⁻³)	2.028, -1.030	3.972, -3.023	4.666, -4.155

Compound	7	11	15
Formula	[Au ₂ Cl ₂ (μ-C ₆ H ₃ -6-F-2-PPh ₂) ₂]	[Au ₂ I ₂ (μ-2-C ₆ F ₄ PPh ₂) ₂]	[Au ₂ (ONO ₂) ₂ (μ-2-C ₆ F ₄ PPh ₂) ₂].CH ₂ Cl ₂
fw	1083.17	1314.19	1269.34
Crystal system	Triclinic	Monoclinic	Monoclinic
Space group	P-1	P2 ₁ /n	P2 ₁ /n
<i>a</i> , Å	9.57140(10)	13.5862(2)	9.3504(3)
<i>b</i> , Å	19.3795(3)	17.8577(3)	19.5747(6)
<i>c</i> , Å	20.7246(4)	15.0048(2)	21.6622(6)
<i>α</i> , deg	72.6120(10)	90	90
<i>β</i> , deg	80.9120(10)	92.5220(10)	98.734(2)
<i>γ</i> , deg	82.9700(10)	90	90
<i>V</i> , Å ³	3610.92(10)	3636.91(9)	3918.9(2)
<i>Z</i>	4	4	4
D _{calc} (Mg m ⁻³)	1.992	2.400	2.151
<i>μ</i> (mm ⁻¹)	8.476	9.912	7.784
T, K	100(2)	200(2)	200(2)
Cryst dims (mm)	0.20 × 0.05 × 0.04	0.17 × 0.10 × 0.04	0.35 × 0.03 × 0.03
Theta range, deg	2.62-27.00	2.72-25.00	2.82-25.00
Reflections collected	74858	65911	9095
unique (<i>R</i> _{int})	15753 (0.0674)	6407(0.0777)	6735(0.0305)
Data / Restraints / Parameters	15753 / 35 / 864	6407 / 0 / 451	6735 / 0 / 532
Final R indices [<i>I</i> > 2σ(<i>I</i>)]	R1 = 0.0376, wR2 = 0.0841	R1 = 0.0249, wR2 = 0.0631	R1 = 0.0423, wR2 = 0.0720
R indices (all data)	R1 = 0.0563, wR2 = 0.0896	R1 = 0.0312, wR2 = 0.0659	R1 = 0.0847, wR2 = 0.0807
Largest diff. peak and hole (e.Å ⁻³)	2.450, -1.945	1.394, -1.835	1.670, -0.960

Compound	16	17	18
Formula	[Au ₂ (OBz) ₂ (μ-2-C ₆ F ₄ PPh ₂) ₂]	[Au ^{II} ₂ (O ₂ CCF ₃) ₂ (μ-2-C ₆ F ₄ PPh ₂) ₂].CH ₂ Cl ₂	[Au ₂ (C ₆ F ₅) ₂ (μ-2-C ₆ F ₄ PPh ₂) ₂]
fw	1345.7	2648.45	1415.74
Crystal system	Monoclinic	Triclinic	Triclinic
Space group	P2 ₁ /n	P-1	P-1
<i>a</i> , Å	12.14090(10)	11.17170(10)	11.2743(3)
<i>b</i> , Å	15.8124(2)	19.9849(2)	13.8378(3)
<i>c</i> , Å	24.6158(3)	21.4899(3)	15.6632(3)
<i>α</i> , deg	90	64.4990(10)	72.6380(10)
<i>β</i> , deg	99.8870(10)	80.8060(10)	72.0350(10)
<i>γ</i> , deg	90	75.6400(10)	86.0370(10)
<i>V</i> , Å ³	4655.48(9)	4187.51(9)	2217.89(9)
<i>Z</i>	4	2	2
D _{calc} (Mg m ⁻³)	1.920	2.100	2.120
<i>μ</i> (mm ⁻¹)	6.444	7.236	6.822
T, K	110(2)	130(2)	100(2)
Cryst dims (mm)	0.27 × 0.10 × 0.10	0.21 × 0.20 × 0.15	0.26 × 0.12 × 0.07
Theta range, deg	2.71-36.00	2.66-27.50	2.70-29.00
Reflections collected	154997	73448	55739
unique (<i>R</i> _{int})	22018 (0.0754)	19224(0.0427)	11780 (0.0559)
Data / Restraints / Parameters	22018 / 0 / 623	19224 / 157 / 1208	11780 / 136 / 733
Final R indices [<i>I</i> > 2σ(<i>I</i>)]	R1 = 0.0312, wR2 = 0.0557	R1 = 0.0337, wR2 = 0.0847	R1 = 0.0332, wR2 = 0.0770
R indices (all data)	R1 = 0.0529, wR2 = 0.0594	R1 = 0.0466, wR2 = 0.0906	R1 = 0.0473, wR2 = 0.0810
Largest diff. peak and hole (e.Å ⁻³)	2.125, -2.019	1.596, -1.617	3.005, -1.953

Compound	19	21	22
Formula	[Au ₂ ^{I,III} (CH ₃) ₂ (μ-2-C ₆ F ₄ PPh ₂) ₂]	[Au ₄ (μ-2-C ₆ F ₄ PPh ₂) ₄]	[Au ₄ (μ-C ₆ H ₃ -5-F-2-PPh ₂) ₄]
fw	1090.46	2412.93	1989.81
Crystal system	Triclinic	Tetragonal	Monoclinic
Space group	P-1	P4 ₂ /n	P2 ₁ /c
<i>a</i> , Å	11.9272(2)	15.9440(3)	14.2878(2)
<i>b</i> , Å	12.2979(2)	15.9440(3)	16.7228(3)
<i>c</i> , Å	14.2430(2)	14.7921(2)	27.8198(4)
α, deg	71.7130(10)	90	90
β, deg	66.9410(10)	90	101.9280(10)
γ, deg	64.2670(10)	90	90
<i>V</i> , Å ³	1705.37	3760.32(11)	6503.52(18)
<i>Z</i>	2	2	4
D _{calc} (Mg m ⁻³)	2.124	2.131	2.032
μ (mm ⁻¹)	8.759	8.192	9.230
T, K	110(2)	110(2)	100(2)
Cryst dimens (mm)	0.29 × 0.14 × 0.09	0.17 × 0.15 × 0.09	0.13 × 0.11 × 0.05
Theta range, deg	2.65-35.00	2.90-35.00	2.55-28.00
Reflections collected	66388	41538	80637
unique (R _{int})	14975 (0.0732)	8284 (0.0415)	15654 (0.0746)
Data / Restraints / Parameters	14975 / 0 / 451	8284 / 25 / 283	15654 / 33 / 805
Final R indices [<i>I</i> > 2σ(<i>I</i>)]	R1 = 0.0363, wR2 = 0.0897	R1 = 0.0318, wR2 = 0.0722	R1 = 0.0355, wR2 = 0.0674
R indices (all data)	R1 = 0.0468, wR2 = 0.0936	R1 = 0.0527, wR2 = 0.0774	R1 = 0.0606, wR2 = 0.0731
Largest diff. peak and hole (e.Å ⁻³)	5.705, -3.880	1.689, -1.669	1.505, -1.756

Compound	24	28	32
Formula	[{Au ₂ Br(μ-C ₆ H ₃ -6-F-2-PPh ₂) ₂ }(C ₆ H ₃ -6-F-2-PPh ₂)AuBr]	[ClAu(μ-2-C ₆ H ₃ -6-F-2-PPh ₂)(κ ² -C ₆ H ₃ -6-F-2-PPh ₂)AuCl]	[Au ₂ Cl ₂ (2,2'-Ph ₂ P-5-F-C ₆ H ₃ C ₆ H ₃ -5-F-PPh ₂)]
fw	1793.98	1108.27	1023.34
Crystal system	Monoclinic	Triclinic	Monoclinic
Space group	P2 ₁ /n	P-1	P2 ₁ /c
<i>a</i> , Å	19.0219(3)	8.84910(10)	11.01700(10)
<i>b</i> , Å	11.9992(2)	11.4657(2)	15.97300(10)
<i>c</i> , Å	26.0829(4)	18.1948(3)	18.1351(2)
α, deg	90	87.2030(10)	90
β, deg	103.3430(10)	77.6010(10)	90.4610(10)
γ, deg	90	86.2500(10)	90
<i>V</i> , Å ³	5792.65(16)	1798.00	3191.21(5)
<i>Z</i>	4	2	4
D _{calc} (Mg m ⁻³)	2.057	2.047	2.130
μ (mm ⁻¹)	9.229	8.574	9.490
T, K	100(2)	100(2)	100(2)
Cryst dimens (mm)	0.25 × 0.17 × 0.07	0.41 × 0.12 × 0.05	0.30 × 0.25 × 0.22
Theta range, deg	2.75-29.00	2.83-35.00	2.79-35.00
Reflections collected	67386	67525	76037
unique (R _{int})	15370 (0.0697)	15839 (0.0700)	14036 (0.0554)
Data / Restraints / Parameters	15370 / 61 / 715	15839 / 27 / 434	14036 / 0 / 397
Final R indices [<i>I</i> > 2σ(<i>I</i>)]	R1 = 0.0413, wR2 = 0.1017	R1 = 0.0340, wR2 = 0.0827	R1 = 0.0266, wR2 = 0.0576
R indices (all data)	R1 = 0.0592, wR2 = 0.1079	R1 = 0.0447, wR2 = 0.0864	R1 = 0.0367, wR2 = 0.0599
Largest diff. peak and hole (e.Å ⁻³)	3.753, -3.555	4.081, -3.527	2.100, -1.949

Compound	33	35	36
Formula	[Au ₂ Br ₂ (2,2'-Ph ₂ P-5-F-C ₆ H ₃ C ₆ H ₃ -5-F-PPh ₂)]	[OAcAu(μ-2-C ₆ F ₄ PPh ₂)(κ ² -2-C ₆ F ₄ PPh ₂)AuOAc]	[(O ₂ NO)Au(μ-2-C ₆ F ₄ PPh ₂)(κ ² -2-C ₆ F ₄ PPh ₂)Au(ONO ₂)]
fw	1112.26	1189.65	1184.41
Crystal system	Monoclinic	Triclinic	Monoclinic
Space group	P2 ₁ /c	P-1	P2 ₁ /c
<i>a</i> , Å	11.03440(10)	10.0844(3)	10.1875(3)
<i>b</i> , Å	16.0528(2)	11.2569(3)	34.2523(12)
<i>c</i> , Å	18.4780(2)	18.2943(5)	10.5338(3)
α, deg	90	92.311(2)	90
β, deg	91.6760(10)	96.760(2)	90.854(2)
γ, deg	90	114.716(2)	90
<i>V</i> , Å ³	3271.66(6)	1864.14(10)	3675.3(2)
<i>Z</i>	4	2	4
D _{calc} (Mg m ⁻³)	2.258	2.119	2.141
μ (mm ⁻¹)	11.536	8.032	8.151
T, K	100(2)	110(2)	110(2)
Cryst dimens (mm)	0.37 × 0.25 × 0.19	0.12 × 0.07 × 0.04	0.21 × 0.19 × 0.10
Theta range, deg	2.83-35.00	2.86-28.50	2.68-27.36
Reflections collected	70789	49598	29664
unique (R _{int})	14374(0.0748)	9396(0.0861)	8226 (0.0790)
Data / Restraints / Parameters	14374 / 0 / 397	9396 / 55 / 559	8226 / 0 / 505
Final R indices [<i>I</i> > 2σ(<i>I</i>)]	R1 = 0.0318, wR2 = 0.0721	R1 = 0.0379, wR2 = 0.0711	R1 = 0.0530, wR2 = 0.1288
R indices (all data)	R1 = 0.0454, wR2 = 0.0756	R1 = 0.0754, wR2 = 0.0786	R1 = 0.0716, wR2 = 0.1368
Largest diff. peak and hole (e.Å ⁻³)	2.685, -2.383	2.017, -1.579	3.913, -2.628

Compound	41	42
Formula	[Cl ₃ Au(μ-2-C ₆ F ₄ PPh ₂)(κ ² -2-C ₆ F ₄ PPh ₂)AuCl]	[Br ₃ Au(μ-2-C ₆ F ₄ PPh ₂)AuBr(κ ² -2-C ₆ F ₄ PPh ₂)]
fw	1287.12	1464.96
Crystal system	Triclinic	Triclinic
Space group	P-1	P-1
<i>a</i> , Å	10.7369(2)	10.9022(3)
<i>b</i> , Å	14.4038(2)	14.5683(4)
<i>c</i> , Å	14.5209(2)	14.5702(4)
α, deg	60.9030(10)	119.3830(10)
β, deg	82.7430(10)	94.2110(10)
γ, deg	88.0100(10)	92.7670(10)
<i>V</i> , Å ³	1945.64(6)	2001.51(10)
<i>Z</i>	2	2
D _{calc} (Mg m ⁻³)	2.197	2.431
μ (mm ⁻¹)	8.094	11.594
T, K	100(2)	100(2)
Cryst dimens (mm)	0.29 × 0.20 × 0.12	0.22 × 0.18 × 0.10
Theta range, deg	2.63-38.00	2.59-33.00
Reflections collected	80292	50246
unique (R _{int})	21176 (0.0631)	15094(0.0611)
Data / Restraints / Parameters	21176 / 0 / 496	15094 / 0 / 497
Final R indices [<i>I</i> > 2σ(<i>I</i>)]	R1 = 0.0338, wR2 = 0.0838	R1 = 0.0493, wR2 = 0.1151
R indices (all data)	R1 = 0.0419, wR2 = 0.0868	R1 = 0.0560, wR2 = 0.1174
Largest diff. peak and hole (e.Å ⁻³)	5.374, -5.879	5.481, -2.992

Syntheses:

(2-Trimethylstannyltetrafluorophenyl)diphenylphosphine).

A solution of 2-BrC₆F₄PPh₂ (16 mmol, 6.6 g) in ether (100 mL) was cooled to -78 °C and treated slowly with a solution of ⁿBuLi (1.6 M in hexanes, 16 mmol, 10.0 mL). After stirring for 30 min, Me₃SnCl (1.0 M in hexanes, 16 mmol, 16.0 mL) was added dropwise to the solution, which was stirred at -78 °C for 2 hours. After being allowed to warm to room temperature, the suspension was hydrolysed and the ether layer separated. The aqueous phase was extracted with ether (3 × 50 mL) and the combined organic phases were dried (MgSO₄). After filtration, the solvent was removed and the gummy solid was recrystallised from hot methanol to give white crystals of the title compound (6.9 g, 87%).

m.p: 77-79 °C. ¹H NMR (CDCl₃): δ 0.50 (s, with ¹¹⁷Sn/¹¹⁹Sn satellites *J* = 56.5 Hz, 9H, SnMe₃), 7.2-7.4 (m, 10H, aromatics). ¹³C NMR (CDCl₃): δ -3.9 (dd, *J* = 4.5, 13.3 Hz with ¹¹⁷Sn/¹¹⁹Sn satellites *J* = 369.5 Hz) together with 128.5 (d, *J* = 6.4 Hz), 128.8 (s), 132.4 (dd, *J* = 1.8, 18.9 Hz), 134.6 (dd, *J* = 2.2, 9.2 Hz) due to the PPh₂ carbons and low intensity peaks at δ 125.5 (m), 140.7 (m), 141.5 (m), 148.7 (m), 150.1 (m), 150.7 (m) due to the C₆F₄ carbons. ³¹P NMR (CDCl₃): δ -0.2 (ddd, *J*_{PF} = 1.6, 2.9, 22.8 Hz with ¹¹⁷Sn/¹¹⁹Sn satellites *J* = 29.4 Hz). ¹⁹F NMR (CDCl₃): δ -119.1 (m), -120.4 (m), -151.3 (m), -153.2 (m). ESI-MS (*m/z*): 499 [*M*+H]⁺. Anal. Calcd. for C₂₁H₁₉F₄PSn: C 50.75, H 3.85, F 15.29. Found: C 51.04, H 3.96, F 15.32.

(2-Bromo-*n*-fluorophenyl)diphenylphosphine (*n* = 3, 4).

To a solution of 2-bromo-3-fluoriodobenzene (16.1 mmol, 4.9 g) and [PdCl₂(NCMe)₂] (0.4 mmol, 0.1 g) in dry toluene (20 mL) was added (trimethylsilyl)diphenylphosphine (17.5 mmol, 4.5 g). The resulting dark solution was stirred at 85 °C for 3 days and then allowed to cool to room temperature. Dichloromethane was added and the solution was washed with saturated aqueous NaHCO₃. The organic layer was separated and the aqueous layer was extracted with CH₂Cl₂ (3 × 50 mL). The combined organic extracts were dried over MgSO₄ and filtered: the solvents were evaporated to give an orange semi-solid. The crude product was passed down a silica-gel column, eluting with toluene/hexane (1:1) to give (2-bromo-3-fluorophenyl)diphenylphosphine as a colourless oil, which was crystallised from hot methanol to afford the title product as a white solid (3.8 g, 66%).

m.p: 139-141 °C. ^1H NMR (CDCl_3): δ 6.50 (m, 1H, aromatic), 7.12 (m, 2H, aromatics), 7.2-7.6 (m, 10H, aromatics). ^{13}C NMR (CDCl_3): δ 116.0 (dd, $J_{\text{FC}} = 20.3$ Hz, $J_{\text{PC}} = 31.1$ Hz), 116.3 (d, $J_{\text{FC}} = 22.9$), 128.4 (d, $J_{\text{PC}} = 7.5$ Hz), 128.7 (d, $J_{\text{PC}} = 7.4$ Hz), 129.2 (s), 129.6 (dd, $J_{\text{FC}} = 1.5$ Hz, $J_{\text{PC}} = 3.3$ Hz), 134.0 (d, $J_{\text{PC}} = 20.5$ Hz), 135.3 (d, $J_{\text{PC}} = 10.5$ Hz), 141.0 (dd, $J_{\text{FC}} = 1.1$ Hz, $J_{\text{PC}} = 14.3$ Hz), 159.1 (dd, $J_{\text{FC}} = 249$ Hz, $J_{\text{PC}} = 5.4$ Hz). ^{31}P NMR (CDCl_3): δ -4.5 (d, $J_{\text{PF}} = 9.4$ Hz). ^{19}F NMR (CDCl_3): δ -105.4 (m). ESI-MS (m/z): 359 $[M+H]^+$. Anal. Calcd. for $\text{C}_{18}\text{H}_{13}\text{BrFP}$: C 60.19, H 3.65, Br 22.25, P 8.62. Found: C 60.18, H 3.82, Br 22.04, P 8.47.

(2-Bromo-4-fluorophenyl)diphenylphosphine was prepared similarly to (2-bromo-3-fluorophenyl)diphenylphosphine and obtained as a colourless solid in 81% yield from 2-bromo-4-fluoroiodobenzene (50.8 mmol, 15.3 g), $[\text{PdCl}_2(\text{NCMe})_2]$ (0.98 mmol, 0.25 g) and (trimethylsilyl)diphenylphosphine (53.8 mmol, 13.9 g).

m.p: 86-88 °C. ^1H NMR (CDCl_3): δ 6.75 (ddd, $J_{\text{HH}} = 8.6$ Hz, $J_{\text{FH}} = 6.4$ Hz, $J_{\text{PH}} = 2.2$ Hz, 1H, aromatic), 6.96 (dt, $J_{\text{HH}} = 2.4, 8.4$ Hz, $J_{\text{FH}} = 8.4$ Hz, 1H, aromatic), 7.2-7.5 (m, 11H, aromatics). ^{13}C NMR (CDCl_3): δ 114.9 (d, $J = 20.2$ Hz), 120.4 (d, $J = 24.2$ Hz), 128.7 (d, $J_{\text{PC}} = 7.3$ Hz), 129.1 (s), 129.9 (dd, $J = 9.1, 33.2$ Hz), 133.8 (d, $J_{\text{PC}} = 29.5$ Hz), 134.4 (dd, $J = 4.1, 12.2$ Hz), 135.6 (d, $J_{\text{PC}} = 2.6$ Hz), 135.7 (s), 162.7 (d, $J = 253$ Hz). ^{31}P NMR (CDCl_3): δ -5.8 (d, $J_{\text{PF}} = 3.7$ Hz). ^{19}F NMR (CDCl_3): δ -111.5 (ddt, $J_{\text{PF}} = 3.1$ Hz, $J_{\text{FH}} = 6.3, 8.2$ Hz). ESI-MS (m/z): 359 $[M+H]^+$. Anal. Calcd. for $\text{C}_{18}\text{H}_{13}\text{BrFP}$: C 60.19, H 3.65, Br 22.25, P 8.62. Found: C 60.52, H 3.79, Br 21.96, P 8.65.

(2-Trimethylstannyl-*n*-fluorophenyl)diphenylphosphine ($n = 3, 4$).

To a solution of (2-bromo-3-fluorophenyl)diphenylphosphine (2.6 mmol, 0.9 g) in ether (50 mL) cooled to -78 °C was added $n\text{BuLi}$ (1.6 M in hexanes, 2.6 mmol, 1.6 mL). The suspension was stirred for 30 min and then Me_3SnCl (1.0 M in hexanes, 2.6 mmol, 2.6 mL) was slowly added. The mixture was stirred at -78 °C for 2 hours and then allowed to warm to room temperature. The resulting suspension was hydrolysed, the organic layer was separated and the aqueous phase was extracted with ether (3×50 mL). The combined organic extracts were dried over MgSO_4 , filtered, and the solvent was evaporated to give a gummy solid which was crystallised from hot methanol to give (2-trimethylstannyl-3-fluorophenyl)diphenylphosphine as a white solid (0.77 g, 68%).

m.p: 58-60 °C. ^1H NMR (CDCl_3): δ 0.48 (t, $J_{\text{PH}} = J_{\text{FH}} = 1.4$ Hz with $^{117}\text{Sn}/^{119}\text{Sn}$ satellites $J = 54.2, 56.5$ Hz, 9H, SnMe_3), 6.6-7.4 (m, 13H, aromatics). ^{13}C NMR (CDCl_3): δ -4.7 (dd, $J = 4.1, 11.2$ Hz with $^{117}\text{Sn}/^{119}\text{Sn}$ satellites $J = 349.9, 366.1$ Hz), 115.1 (d, $J_{\text{FC}} = 25.3$ Hz, with $^{117}\text{Sn}/^{119}\text{Sn}$ satellites $J = 16.2$ Hz), 128.8 (d, $J_{\text{PC}} = 5.0$ Hz), 128.9 (s), 129.0 (d, $J_{\text{PC}} = 2.9$ Hz with $^{117}\text{Sn}/^{119}\text{Sn}$ satellites $J = 34.4$ Hz), 131.0 (d, $J_{\text{PC}} = 9.2$ Hz), 133.5 (d, $J_{\text{PC}} = 18.6$ Hz), 136.9 (dd, $J_{\text{PC}/\text{FC}} = 40.7, 62.1$ Hz), 138.0 (d, $J_{\text{PC}} = 25.3$

Hz with $^{117}\text{Sn}/^{119}\text{Sn}$ satellites $J = 16.2$ Hz), 148.0 (dd, $J_{\text{PC/FC}} = 6.1, 11.1$ Hz with $^{117}\text{Sn}/^{119}\text{Sn}$ satellites $J = 22.9$ Hz), 167.9 (dd, $J_{\text{FC}} = 237.7$ Hz, $J_{\text{PC}} = 22.8$ Hz). ^{31}P NMR (CDCl_3): δ -2.5 (d, $J_{\text{PF}} = 1.6$ Hz with $^{117}\text{Sn}/^{119}\text{Sn}$ satellites $J = 37.9, 40.6$ Hz). ^{19}F NMR (CDCl_3): δ -91.4 (br s, with $^{117}\text{Sn}/^{119}\text{Sn}$ satellites $J = 60.4$ Hz). ESI-MS (m/z): 445 $[\text{M}+\text{H}]^+$. Anal. Calcd. for $\text{C}_{21}\text{H}_{22}\text{FPSn}$: C 56.93, H 5.00, F 4.29, P 6.99. Found: C 57.01, H 5.03, F 4.15, P 6.87.

(2-Trimethylstannyl-4-fluorophenyl)diphenylphosphine was made analogously to (2-trimethylstannyl-3-fluorophenyl)diphenylphosphine on the same scale in 85% yield.

m.p: 77-79 °C. ^1H NMR: δ 0.32 (d, $J = 1.2$ Hz, with $^{117}\text{Sn}/^{119}\text{Sn}$ satellites $J = 53.1, 55.4$ Hz, 9H, SnMe_3), 6.6-7.5 (m, 13H, aromatics). ^{13}C NMR: δ -6.1 (d, $J = 10.3$ Hz with $^{117}\text{Sn}/^{119}\text{Sn}$ satellites $J = 331.7, 352.2$ Hz), 116.4 (d, $J = 22.5$ Hz), 122.8 (dd, $J = 17.5, 21.5$ Hz with $^{117}\text{Sn}/^{119}\text{Sn}$ satellites $J = 45.5, 79.7$ Hz), 128.7 (d, $J = 3.2$ Hz), 128.9 (s), 133.5 (d, $J = 18.4$ Hz), 136.7 (d, $J = 6.2$ Hz with $^{117}\text{Sn}/^{119}\text{Sn}$ satellites $J = 38.9, 51.3$ Hz), 138.3 (d, $J = 10.2$ Hz), 140.4 (t, $J = 2.0$ Hz, with $^{117}\text{Sn}/^{119}\text{Sn}$ satellites $J = 34.73, 41.1$ Hz), 156.6 (dd, $J = 2.9, 70.7$ Hz), 163.7 (d, $J = 253.9$ Hz). ^{31}P NMR: δ -4.2 (d, $J_{\text{PF}} = 5.8$ Hz with $^{117}\text{Sn}/^{119}\text{Sn}$ satellites $J = 30.1, 41.6$ Hz). ^{19}F NMR (CDCl_3): δ -112.6 (t, $J = 6.59$ Hz), ESI-MS (m/z): 445 $[\text{M}+\text{H}]^+$. Anal. Calcd. for $\text{C}_{21}\text{H}_{22}\text{FPSn}$: C 56.93, H 5.00, F 4.29, P 6.99. Found: C 56.16, H 5.24, F 3.97, P 6.31.

5-Fluoro-substituted digold(I) complex $[\text{Au}_2(\mu\text{-C}_6\text{H}_3\text{-5-F-2-PPh}_2)_2]$ **3**.

A solution of 2-Br-4-FC₆H₃PPh₂ (1.6 mmol, 0.6 g) in ether (20 mL) was cooled to -78 °C and $n\text{BuLi}$ (1.6 M in hexanes, 1.6 mmol, 1.0 mL) was added slowly. The mixture was stirred for 30 min and a suspension of $[\text{AuBr}(\text{AsPh}_3)]$ (1.6 mmol, 0.97 g) in ether (20 mL) was added via cannula. The resulting mixture was stirred at -78 °C for 2 hours and then allowed to warm to room temperature overnight. The white solid was isolated by filtration and washed successively with ether (10 mL), methanol (10 mL) and hexane (20 mL). The crude product was extracted with hot dichloromethane and the extract was filtered through Celite. Evaporation of the solution gave $[\text{Au}_2(\mu\text{-C}_6\text{H}_3\text{-5-F-2-PPh}_2)_2]$ as a colourless solid (0.88 g, 55%).

^1H NMR: δ 6.7-8.1 (m, 26H, aromatics). ESI-MS (m/z): 953 $[\text{M}+\text{H}]^+$.

Alternatively, an analogous reaction to that for the preparation of the digold(I) complex $[\text{Au}_2(\mu\text{-C}_6\text{H}_3\text{-6-F-2-PPh}_2)_2]$, using 2-Me₃Sn-4-FC₆H₃PPh₂ (2.3 mmol, 1.0 g) and $[\text{AuCl}(\text{tht})]$ (2.3 mmol, 0.7 g), gave a mixture of the dinuclear complex $[\text{Au}_2(\mu\text{-C}_6\text{H}_3\text{-5-F-2-PPh}_2)_2]$ and tetranuclear complex $[\text{Au}_4(\mu\text{-C}_6\text{H}_3\text{-5-F-2-PPh}_2)_4]$. The ^{31}P NMR spectrum of this solid showed two triplet resonances at δ 40.6 (t, $J = 6.0$ Hz) and 36.1 (t, $J = 5.2$ Hz). The former was always the major peak (*ca.* 70%) and is assigned to the tetramer.

ESI-mass spectrum of this mixture showed expected the $[M+H]^+$ ion peaks due to the dimer and tetramer at m/z 953 and 1905, respectively.

6-Fluoro-substituted digold(I) complex $[\text{Au}_2(\mu\text{-C}_6\text{H}_3\text{-6-F-2-PPh}_2)_2]$ **4.**

To a solution of 2-Me₃Sn-3-FC₆H₃PPh₂ (2.26 mmol, 1.0 g) in dichloromethane (40 mL) was added [AuCl(tht)] (2.26 mmol, 0.72 g) and the mixture was refluxed for 24 hours. The volume was reduced and hexane added to precipitate the title complex as a white solid which was isolated by filtration, washed with hexane and dried *in vacuo* (1.6 g, 75%).

¹H NMR: δ 6.9-7.6 (m, 26H, aromatics). ESI-MS (m/z): 953 $[M+H]^+$.

Alternatively, an analogous reaction to that for the preparation of the digold(I) complex $[\text{Au}_2(\mu\text{-2-C}_6\text{F}_4\text{PPh}_2)_2]$ (**1**), using 2-Br-3-FC₆H₃PPh₂ (2.8 mmol, 1.0 g), ⁿBuLi (1.6 M in hexanes, 2.8 mmol, 1.7 mL) and [AuBr(AsPh₃)] (2.8 mmol, 1.6 g), gave a mixture of the dinuclear complex $[\text{Au}_2(\mu\text{-C}_6\text{H}_3\text{-6-F-2-PPh}_2)_2]$ and tetranuclear species $[\text{Au}_4(\mu\text{-C}_6\text{H}_3\text{-6-F-2-PPh}_2)_4]$ in 78% yield. The ³¹P NMR spectrum of this solid showed a doublet of doublets at δ 39.0 ($J = 1.2, 2.4$ Hz) due to the dimer and a doublet of multiplets at δ 41.1 ($J = ca. 5$ Hz) due to the tetramer; the former peak was always more intense (*ca.* 70%). The ESI-mass spectrum of this mixture showed the expected $[M+H]^+$ ion peaks due to the dimer and tetramer at m/z 953 and 1905, respectively.