Supporting Information

Synthesis and characterization of *cis*-bisdiphenylphosphinoethene gold(I) complexes

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Table of Content:

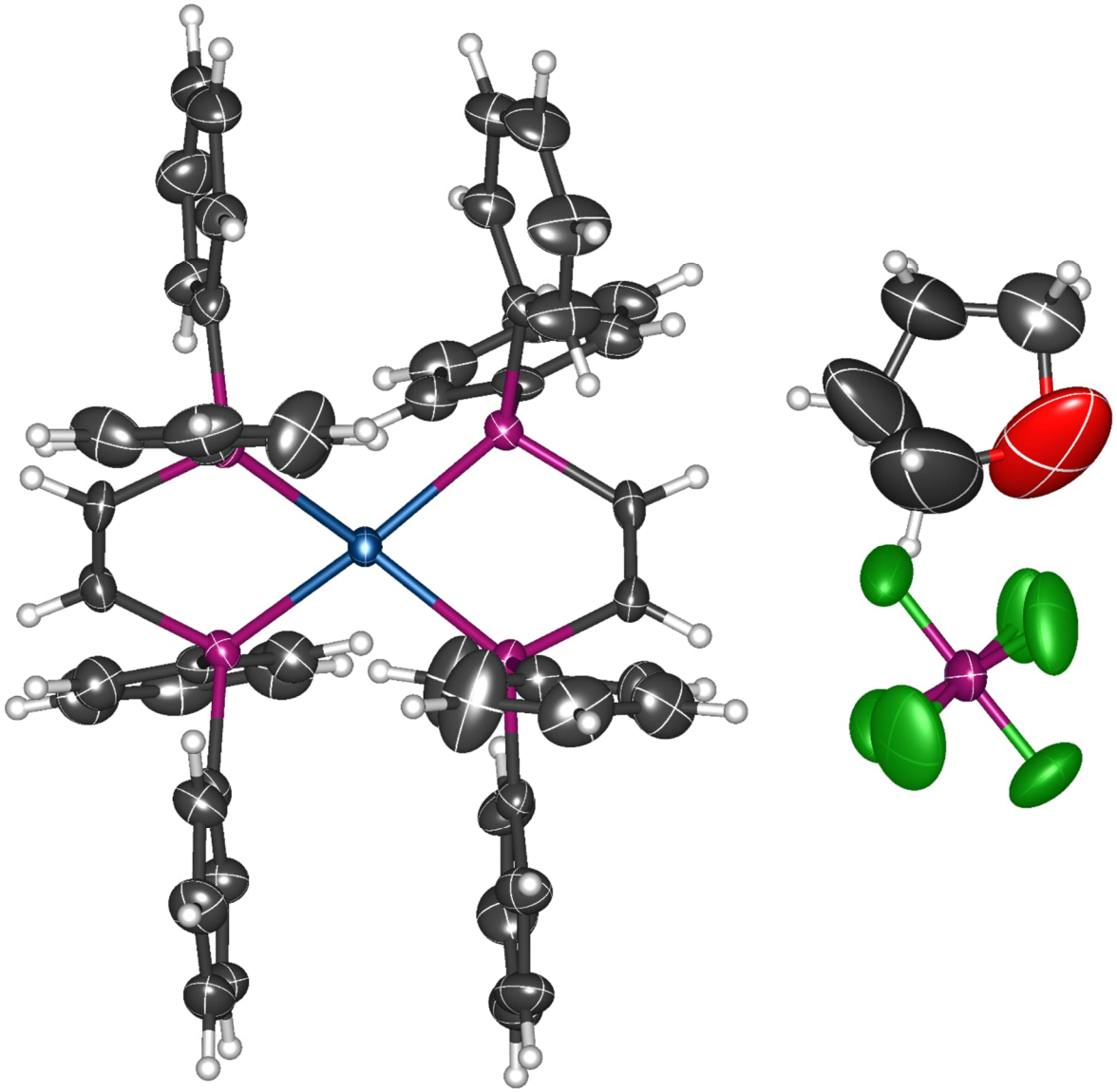

Figure S 1: Solid state structure of 1-PF_6. Thermal ellipsoids are plotted at a 50% probability level. Further crystallographic details are found in Table 19.

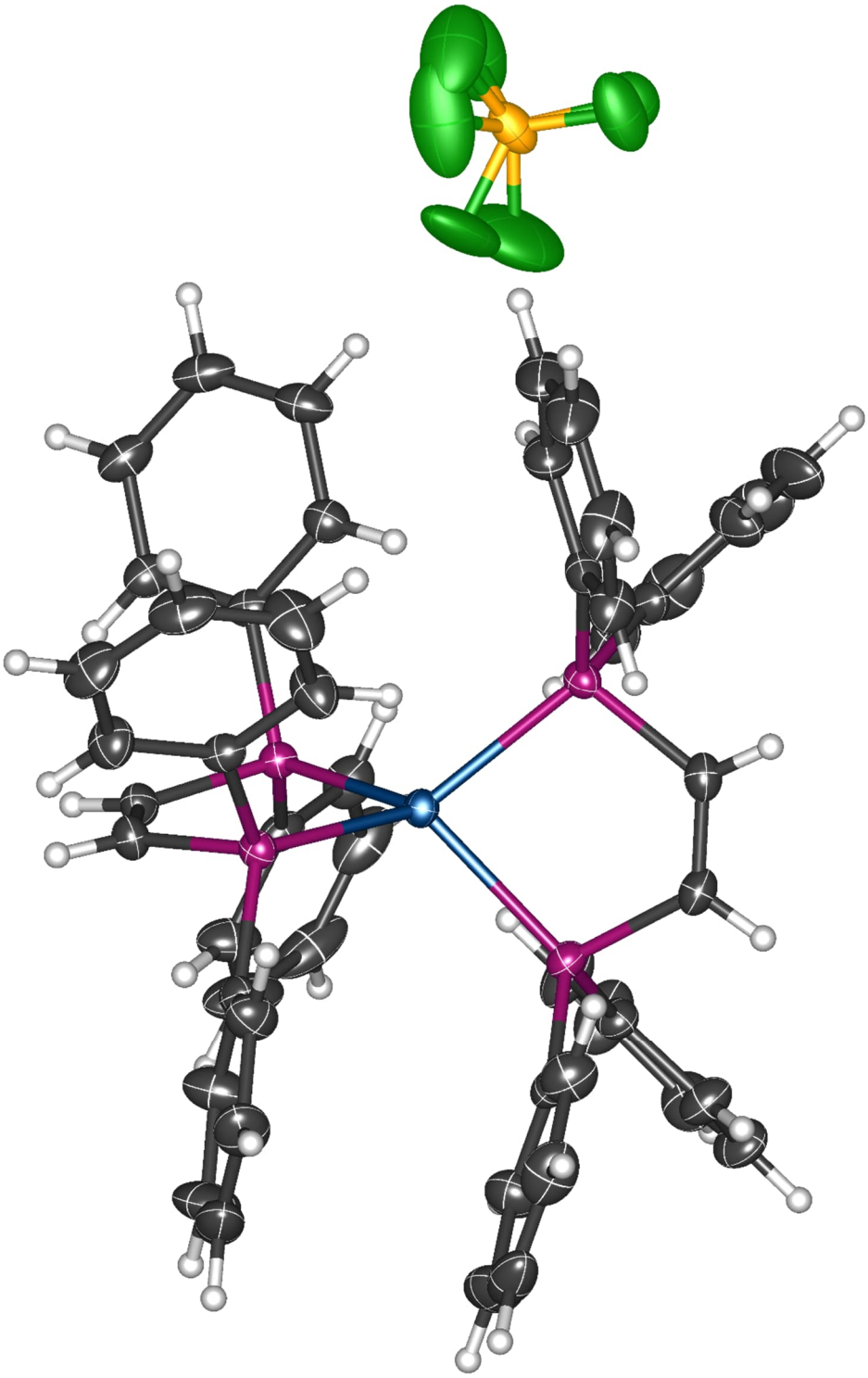

Figure S 2: Solid state structure of 1-BF_4. Thermal ellipsoids are plotted at a 50% probability level. Further crystallographic details are found in Table 14.

Compound 1-Cl

Table 1 Crystal data and structure refinement for 1-Cl

Identification code	**1-Cl**
Empirical formula	$C_{52}H_{44}AuP_4Cl,4(CHCl_3)$
Formula weight	1502.64
Temperature/K	180
Crystal system	monoclinic
Space group	C2/c
a/Å	25.617(3)
b/Å	13.6294(11)
c/Å	22.025(2)
α/°	90
β/°	125.118(2)
γ/°	90
Volume/Å^3	6290.1(11)
Z	4
ρ_{calc}g/cm^3	1.587
μ/mm^{-1}	3.029
F(000)	2976.0
Crystal size/mm^3	0.3 × 0.25 × 0.2
Radiation	MoK$_\alpha$ (λ = 0.71073)
2Θ range for data collection/°	3.564 to 60.674
Index ranges	-36 ≤ h ≤ 36, -19 ≤ k ≤ 19, -31 ≤ l ≤ 31
Reflections collected	110120
Independent reflections	9406 [R_{int} = 0.0510, R_{sigma} = 0.0246]
Data/restraints/parameters	9406/0/335
Goodness-of-fit on F^2	1.026
Final R indexes [I>=2σ (I)]	R_1 = 0.0243, wR_2 = 0.0515
Final R indexes [all data]	R_1 = 0.0313, wR_2 = 0.0545
Largest diff. peak/hole / e Å^{-3}	1.05/-0.90

Table 2 Bond Lengths for 1-Cl

Atom	Atom	Length/Å	Atom	Atom	Length/Å
Au1	P1^1	2.3748(5)	C1	C1^1	1.344(4)
Au1	P1	2.3749(5)	C8	C12	1.394(3)
Au1	P2^1	2.3715(5)	C8	C9	1.390(3)
Au1	P2	2.3716(5)	C29	C30	1.386(4)
P1	C2	1.829(2)	C3	C4	1.390(3)
P1	C1	1.8173(19)	C12	C00L	1.387(3)
P1	C8	1.813(2)	C33	C32	1.388(3)
P2	C21	1.815(2)	C00L	C11	1.376(4)
P2	C28	1.822(2)	C22	C23	1.386(4)
P2	C22	1.816(2)	C22	C27	1.396(3)

Table 2 Bond Lengths for 1-Cl

Atom	Atom	Length/Å	Atom	Atom	Length/Å
Cl1S	C1S	1.759(2)	C9	C10	1.398(3)
Cl3S	C1S	1.770(2)	C23	C24	1.390(4)
Cl2S	C1S	1.748(2)	C7	C6	1.389(4)
Cl5S	C2S	1.760(3)	C4	C5	1.371(4)
Cl4S	C2S	1.762(3)	C30	C31	1.366(4)
Cl6S	C2S	1.756(3)	C32	C31	1.379(4)
C21	C21[1]	1.330(4)	C24	C25	1.385(5)
C2	C3	1.395(3)	C26	C27	1.380(4)
C2	C7	1.380(3)	C26	C25	1.370(5)
C28	C29	1.388(3)	C5	C6	1.375(5)
C28	C33	1.394(3)	C10	C11	1.371(4)

[1]1-X,+Y,1/2-Z

Table 3 Bond Angles for1-Cl

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
P1[1]	Au1	P1	86.53(2)	C30	C29	C28	120.1(2)
P2[1]	Au1	P1[1]	130.528(19)	C4	C3	C2	120.1(2)
P2	Au1	P1	130.528(19)	C00L	C12	C8	120.7(2)
P2	Au1	P1[1]	114.248(19)	Cl1S	C1S	Cl3S	109.54(12)
P2[1]	Au1	P1	114.247(18)	Cl2S	C1S	Cl1S	111.54(14)
P2[1]	Au1	P2	86.54(3)	Cl2S	C1S	Cl3S	110.08(12)
C2	P1	Au1	116.95(7)	C32	C33	C28	120.1(2)
C1	P1	Au1	104.98(6)	C11	C00L	C12	120.0(2)
C1	P1	C2	101.60(9)	C23	C22	P2	118.94(17)
C8	P1	Au1	119.97(7)	C23	C22	C27	119.0(2)
C8	P1	C2	105.21(10)	C27	C22	P2	122.1(2)
C8	P1	C1	106.08(9)	C8	C9	C10	119.8(2)
C21	P2	Au1	104.78(7)	C22	C23	C24	120.4(3)
C21	P2	C28	101.26(10)	C2	C7	C6	120.3(3)
C21	P2	C22	103.94(11)	C5	C4	C3	120.2(3)
C28	P2	Au1	116.60(7)	C31	C30	C29	120.8(3)
C22	P2	Au1	122.00(8)	C31	C32	C33	120.1(3)
C22	P2	C28	105.51(10)	C25	C24	C23	119.7(3)
C21[1]	C21	P2	121.94(7)	C25	C26	C27	120.5(3)
C3	C2	P1	117.54(17)	Cl5S	C2S	Cl4S	110.01(17)
C7	C2	P1	123.46(18)	Cl6S	C2S	Cl5S	109.58(16)
C7	C2	C3	119.0(2)	Cl6S	C2S	Cl4S	110.79(16)
C29	C28	P2	122.14(18)	C4	C5	C6	120.0(2)
C29	C28	C33	118.9(2)	C11	C10	C9	120.6(3)
C33	C28	P2	118.85(17)	C30	C31	C32	119.9(2)
C1[1]	C1	P1	121.66(6)	C10	C11	C00L	120.1(2)

Table 3 Bond Angles for1-Cl

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
C12	C8	P1	117.85(16)	C26	C27	C22	120.2(3)
C9	C8	P1	123.15(17)	C26	C25	C24	120.2(3)
C9	C8	C12	118.8(2)	C5	C6	C7	120.3(3)

[1]1-X,+Y,1/2-Z

Table 4 Torsion Angles for 1-Cl

A	B	C	D	Angle/°	A	B	C	D	Angle/°
Au1	P1	C2	C3	37.68(19)	C28	C33	C32	C31	1.5(4)
Au1	P1	C2	C7	-143.5(2)	C1	P1	C2	C3	-75.93(18)
Au1	P1	C1	C1[1]	-3.9(3)	C1	P1	C2	C7	102.9(2)
Au1	P1	C8	C12	69.39(19)	C1	P1	C8	C12	-172.13(17)
Au1	P1	C8	C9	-106.10(19)	C1	P1	C8	C9	12.4(2)
Au1	P2	C21	C21[1]	-1.3(3)	C8	P1	C2	C3	173.65(17)
Au1	P2	C28	C29	-111.71(18)	C8	P1	C2	C7	-7.5(2)
Au1	P2	C28	C33	64.76(19)	C8	P1	C1	C1[1]	-131.9(2)
Au1	P2	C22	C23	21.6(2)	C8	C12	C00L	C11	0.8(4)
Au1	P2	C22	C27	-156.82(19)	C8	C9	C10	C11	1.1(4)
P1	C2	C3	C4	179.27(19)	C29	C28	C33	C32	-1.2(3)
P1	C2	C7	C6	-179.9(2)	C29	C30	C31	C32	-0.6(5)
P1	C8	C12	C00L	-177.8(2)	C3	C2	C7	C6	-1.1(4)
P1	C8	C9	C10	176.6(2)	C3	C4	C5	C6	-1.5(4)
P2	C28	C29	C30	176.4(2)	C12	C8	C9	C10	1.2(4)
P2	C28	C33	C32	-177.77(19)	C12	C00L	C11	C10	1.5(4)
P2	C22	C23	C24	-178.1(2)	C33	C28	C29	C30	0.0(4)
P2	C22	C27	C26	176.7(2)	C33	C32	C31	C30	-0.6(4)
C21	P2	C28	C29	135.31(19)	C22	P2	C21	C21[1]	-130.4(3)
C21	P2	C28	C33	-48.23(19)	C22	P2	C28	C29	27.2(2)
C21	P2	C22	C23	139.3(2)	C22	P2	C28	C33	-156.29(18)
C21	P2	C22	C27	-39.1(2)	C22	C23	C24	C25	1.4(5)
C2	P1	C1	C1[1]	118.4(2)	C9	C8	C12	C00L	-2.1(4)
C2	P1	C8	C12	-64.95(19)	C9	C10	C11	C00L	-2.4(5)
C2	P1	C8	C9	119.6(2)	C23	C22	C27	C26	-1.7(4)
C2	C3	C4	C5	0.9(4)	C23	C24	C25	C26	-1.9(5)
C2	C7	C6	C5	0.5(5)	C7	C2	C3	C4	0.4(4)
C28	P2	C21	C21[1]	120.4(3)	C4	C5	C6	C7	0.8(5)
C28	P2	C22	C23	-114.5(2)	C27	C22	C23	C24	0.4(4)
C28	P2	C22	C27	67.0(2)	C27	C26	C25	C24	0.6(5)

Table 4 Torsion Angles for 1-Cl

A	B	C	D	Angle/°	A	B	C	D	Angle/°
C28	C29	C30	C31	0.9(4)	C25	C26	C27	C22	1.2(5)

[1]1-X,+Y,1/2-Z

Crystal structure determination of [1-Cl]

Crystal Data for $C_{56}H_{48}AuCl_{13}P_4$ (M =1502.64 g/mol): monoclinic, space group C2/c (no. 15), a = 25.617(3) Å, b = 13.6294(11) Å, c = 22.025(2) Å, β = 125.118(2)°, V = 6290.1(11) Å^3, Z = 4, T = 180 K, μ(MoKα) = 3.029 mm^{-1}, *Dcalc* = 1.587 g/cm^3, 110120 reflections measured (3.564° ≤ 2Θ ≤ 60.674°), 9406 unique (R_{int} = 0.0510, R_{sigma} = 0.0246) which were used in all calculations. The final R_1 was 0.0243 (I > 2σ(I)) and wR_2 was 0.0545 (all data).

Refinement model description

Number of restraints - 0, number of constraints - unknown.

Details:

```
1. Fixed Uiso
 At 1.2 times of:
  All C(H) groups
2.a Ternary CH refined with riding coordinates:
 C1S(H1S), C2S(H2S)
2.b Aromatic/amide H refined with riding coordinates:
 C21(H21), C1(H1), C29(H29), C3(H3), C12(H12), C33(H33), C00L(H00L), C9(H9),
 C23(H23), C7(H7), C4(H4), C30(H30), C32(H32), C24(H24), C26(H26), C5(H5),
 C10(H10), C31(H31), C11(H11), C27(H27), C25(H25), C6(H6)
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Compound 2

Table 5 Crystal data and structure refinement for 2.

Identification code	**2**
Empirical formula	$C_{26}H_{22}Au_2Cl_2P_2$
Formula weight	861.21
Temperature/K	180
Crystal system	monoclinic
Space group	Cc
a/Å	13.1726(10)
b/Å	12.8043(10)
c/Å	15.2893(12)
α/°	90
β/°	100.9060(10)
γ/°	90
Volume/Å^3	2532.2(3)
Z	4
ρ_{calc}g/cm^3	2.259
μ/mm^{-1}	11.925
F(000)	1600.0
Crystal size/mm^3	0.13 × 0.12 × 0.1
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	4.916 to 54.428
Index ranges	-16 ≤ h ≤ 16, -16 ≤ k ≤ 16, -19 ≤ l ≤ 19
Reflections collected	13500
Independent reflections	5477 [R_{int} = 0.0213, R_{sigma} = 0.0432]
Data/restraints/parameters	5477/2/289
Goodness-of-fit on F^2	0.715
Final R indexes [I>=2σ (I)]	R_1 = 0.0149, wR_2 = 0.0320
Final R indexes [all data]	R_1 = 0.0156, wR_2 = 0.0323
Largest diff. peak/hole / e Å^{-3}	0.89/-0.37
Flack parameter	0.015(3)

Table 6 Bond Lengths for 2.

Atom	Atom	Length/Å	Atom	Atom	Length/Å
Au1	Au02	3.0313(3)	C20	C15	1.395(8)
Au1	P1	2.2370(13)	C1	C14	1.333(7)
Au1	Cl1	2.2937(14)	C7	C6	1.397(9)
Au02	Cl2	2.2990(14)	C13	C12	1.379(8)
Au02	P2	2.2305(14)	C18	C19	1.378(9)
P1	C8	1.810(5)	C18	C17	1.379(9)
P1	C2	1.816(5)	C3	C4	1.384(9)
P1	C1	1.810(5)	C21	C26	1.397(9)
P2	C14	1.820(5)	C21	C22	1.389(8)

Table 6 Bond Lengths for 2.

Atom	Atom	Length/Å	Atom	Atom	Length/Å
P2	C21	1.810(6)	C17	C16	1.391(8)
P2	C15	1.816(5)	C16	C15	1.388(8)
C9	C10	1.377(8)	C12	C11	1.379(8)
C9	C8	1.388(7)	C26	C25	1.392(10)
C10	C11	1.380(8)	C22	C23	1.378(10)
C8	C13	1.404(8)	C6	C5	1.357(12)
C2	C7	1.379(8)	C23	C24	1.355(12)
C2	C3	1.391(8)	C25	C24	1.393(12)
C20	C19	1.387(9)	C4	C5	1.381(12)

Table 7 Bond Angles for 2.

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
P1	Au1	Au02	79.24(3)	C19	C20	C15	119.6(6)
P1	Au1	Cl1	172.76(5)	C14	C1	P1	126.6(4)
Cl1	Au1	Au02	107.96(4)	C2	C7	C6	119.1(6)
Cl2	Au02	Au1	86.73(4)	C12	C13	C8	120.2(6)
P2	Au02	Au1	100.42(4)	C19	C18	C17	119.7(6)
P2	Au02	Cl2	172.84(6)	C4	C3	C2	119.9(6)
C8	P1	Au1	110.65(17)	C18	C19	C20	120.7(6)
C8	P1	C2	103.4(2)	C1	C14	P2	128.6(4)
C2	P1	Au1	117.86(19)	C26	C21	P2	120.0(5)
C1	P1	Au1	115.72(18)	C22	C21	P2	119.7(5)
C1	P1	C8	105.3(2)	C22	C21	C26	119.8(6)
C1	P1	C2	102.5(2)	C18	C17	C16	120.5(6)
C14	P2	Au02	119.29(18)	C15	C16	C17	119.7(5)
C21	P2	Au02	115.33(19)	C20	C15	P2	116.8(4)
C21	P2	C14	98.4(2)	C16	C15	P2	123.5(4)
C21	P2	C15	106.1(3)	C16	C15	C20	119.8(5)
C15	P2	Au02	110.02(18)	C11	C12	C13	120.0(5)
C15	P2	C14	106.4(2)	C25	C26	C21	119.0(7)
C10	C9	C8	121.1(5)	C23	C22	C21	120.4(7)
C9	C10	C11	119.5(5)	C12	C11	C10	120.7(5)
C9	C8	P1	119.4(4)	C5	C6	C7	120.6(6)
C9	C8	C13	118.5(5)	C24	C23	C22	120.1(7)
C13	C8	P1	121.9(4)	C26	C25	C24	119.8(7)
C7	C2	P1	120.8(4)	C5	C4	C3	119.6(7)
C7	C2	C3	120.1(5)	C6	C5	C4	120.7(6)
C3	C2	P1	119.0(4)	C23	C24	C25	120.9(7)

Table 8 Torsion Angles for 2.

A	B	C	D	Angle/°	A	B	C	D	Angle/°
Au1	P1	C8	C9	-14.0(5)	C1	P1	C2	C7	-25.1(5)
Au1	P1	C8	C13	171.7(4)	C1	P1	C2	C3	158.8(5)
Au1	P1	C2	C7	-153.4(4)	C7	C2	C3	C4	-0.5(10)
Au1	P1	C2	C3	30.6(5)	C7	C6	C5	C4	0.2(13)
Au1	P1	C1	C14	67.9(5)	C13	C12	C11	C10	0.3(9)
Au02	P2	C14	C1	-0.7(6)	C18	C17	C16	C15	-0.3(9)
Au02	P2	C21	C26	156.0(5)	C3	C2	C7	C6	-0.2(9)
Au02	P2	C21	C22	-31.9(6)	C3	C4	C5	C6	-0.9(13)
Au02	P2	C15	C20	-53.8(5)	C19	C20	C15	P2	-179.6(5)
Au02	P2	C15	C16	125.5(4)	C19	C20	C15	C16	1.0(8)
P1	C8	C13	C12	174.6(5)	C19	C18	C17	C16	0.8(9)
P1	C2	C7	C6	-176.2(5)	C14	P2	C21	C26	-76.0(6)
P1	C2	C3	C4	175.6(5)	C14	P2	C21	C22	96.2(5)
P1	C1	C14	P2	-10.4(7)	C14	P2	C15	C20	175.7(4)
P2	C21	C26	C25	174.5(6)	C14	P2	C15	C16	-5.0(5)
P2	C21	C22	C23	-173.9(6)	C21	P2	C14	C1	-126.0(5)
C9	C10	C11	C12	-0.3(9)	C21	P2	C15	C20	71.6(5)
C9	C8	C13	C12	0.2(9)	C21	P2	C15	C16	-109.1(5)
C10	C9	C8	P1	-174.8(4)	C21	C26	C25	C24	-1.3(12)
C10	C9	C8	C13	-0.2(8)	C21	C22	C23	C24	0.1(12)
C8	P1	C2	C7	84.2(5)	C17	C18	C19	C20	-0.3(10)
C8	P1	C2	C3	-91.8(5)	C17	C16	C15	P2	-179.9(4)
C8	P1	C1	C14	-169.6(5)	C17	C16	C15	C20	-0.6(8)
C8	C9	C10	C11	0.3(8)	C15	P2	C14	C1	124.4(5)
C8	C13	C12	C11	-0.2(9)	C15	P2	C21	C26	33.9(6)
C2	P1	C8	C9	113.1(4)	C15	P2	C21	C22	-154.0(5)
C2	P1	C8	C13	-61.2(5)	C15	C20	C19	C18	-0.6(9)
C2	P1	C1	C14	-61.7(5)	C26	C21	C22	C23	-1.8(11)
C2	C7	C6	C5	0.4(11)	C26	C25	C24	C23	-0.3(13)
C2	C3	C4	C5	1.1(11)	C22	C21	C26	C25	2.4(11)
C1	P1	C8	C9	-139.7(4)	C22	C23	C24	C25	0.9(13)
C1	P1	C8	C13	45.9(5)					

Crystal structure determination of [2]

Crystal Data for $C_{26}H_{22}Au_2Cl_2P_2$ (M =861.21 g/mol): monoclinic, space group Cc (no. 9), a = 13.1726(10) Å, b = 12.8043(10) Å, c = 15.2893(12) Å, β = 100.9060(10)°, V = 2532.2(3) Å^3, Z = 4, T = 180 K, μ(MoKα) = 11.925 mm^{-1}, *Dcalc* = 2.259 g/cm^3, 13500 reflections measured (4.916° ≤ 2Θ ≤ 54.428°), 5477 unique (R_{int} = 0.0213, R_{sigma} = 0.0432) which were used in all calculations. The final R_1 was 0.0149 (I > 2σ(I)) and wR_2 was 0.0323 (all data).

Refinement model description

Number of restraints - 2, number of constraints - unknown.

Details:

```
1. Fixed Uiso
 At 1.2 times of:
  All C(H) groups
2.a Aromatic/amide H refined with riding coordinates:
```

C9(H9), C10(H10), C20(H20), C1(H1), C7(H7), C13(H13), C18(H18), C3(H3),
C19(H19), C14(H14), C17(H17), C16(H16), C12(H12), C26(H26), C22(H22), C11(H11),
C6(H6), C23(H23), C25(H25), C4(H4), C5(H5), C24(H24)

Compound 3

Table 9 Crystal data and structure refinement for 3.

Identification code	**3**
Empirical formula	$C_{54}H_{44}Au_2F_6O_6P_4S_2$
Formula weight	1484.82
Temperature/K	180
Crystal system	triclinic
Space group	P-1
a/Å	10.8708(5)
b/Å	11.0738(5)
c/Å	11.7702(5)
α/°	76.6130(13)
β/°	83.5313(14)
γ/°	74.0031(14)
Volume/Å^3	1323.22(10)
Z	1
ρ_{calc}g/cm^3	1.863
μ/mm^{-1}	5.808
F(000)	720.0
Crystal size/mm^3	0.15 × 0.12 × 0.1
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	3.562 to 59.392
Index ranges	-15 ≤ h ≤ 15, -15 ≤ k ≤ 15, -16 ≤ l ≤ 16
Reflections collected	50095
Independent reflections	7504 [R_{int} = 0.0681, R_{sigma} = 0.0460]
Data/restraints/parameters	7504/125/411
Goodness-of-fit on F^2	1.135
Final R indexes [I>=2σ (I)]	R_1 = 0.0386, wR_2 = 0.0714
Final R indexes [all data]	R_1 = 0.0494, wR_2 = 0.0745
Largest diff. peak/hole / e Å^{-3}	1.52/-1.45

Table 10 Bond Lengths for 3.

Atom	Atom	Length/Å	Atom	Atom	Length/Å
P1	C21	1.811(4)	C22	C27	1.394(7)
P1	C28	1.810(5)	C6	C5	1.371(8)
P1	C22	1.793(5)	C6	C7	1.386(7)
P1	Au1	2.3137(13)	C32	C33	1.383(8)
P1	Au1A	2.865(4)	C32	C31	1.366(8)
P2	C2	1.809(5)	C24	C25	1.380(8)
P2	C8	1.817(5)	C5	C4	1.369(8)
P2	C1	1.809(5)	C27	C26	1.390(8)

Table 10 Bond Lengths for 3.

Atom	Atom	Length/Å	Atom	Atom	Length/Å
P2	Au1[1]	2.3474(14)	C26	C25	1.356(9)
P2	Au1A[1]	1.791(4)	C11	C10	1.370(10)
S1S	O1S	1.428(13)	C30	C29	1.395(7)
S1S	O3S	1.439(8)	C30	C31	1.372(8)
S1S	O2S	1.431(7)	C9	C10	1.390(8)
S1S	C1S	1.803(8)	F3S	C1S	1.304(12)
C21	C1	1.322(6)	F2S	C1S	1.329(10)
C3	C2	1.371(7)	F1S	C1S	1.353(12)
C3	C4	1.379(8)	Au1	Au1[1]	2.9908(4)
C28	C33	1.387(7)	Au1A	Au1A[1]	3.051(4)
C28	C29	1.381(7)	O1T	S1T	1.430(14)
C2	C7	1.397(6)	S1T	O3T	1.436(16)
C23	C22	1.396(7)	S1T	O2T	1.429(18)
C23	C24	1.380(7)	S1T	C1T	1.794(16)
C8	C9	1.398(7)	C1T	F3T	1.31(2)
C8	C13	1.382(7)	C1T	F2T	1.33(2)
C12	C11	1.372(10)	C1T	F1T	1.34(2)
C12	C13	1.377(8)			

[1]1-X,-Y,1-Z

Table 11 Bond Angles for 3.

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
C21	P1	Au1	112.94(15)	C31	C32	C33	120.1(6)
C21	P1	Au1A	113.90(15)	C25	C24	C23	120.4(6)
C28	P1	C21	102.9(2)	C4	C5	C6	120.1(5)
C28	P1	Au1	107.00(16)	C26	C27	C22	119.1(5)
C28	P1	Au1A	104.72(16)	C25	C26	C27	120.8(6)
C22	P1	C21	107.4(2)	C6	C7	C2	119.4(5)
C22	P1	C28	106.4(2)	C10	C11	C12	119.2(5)
C22	P1	Au1	118.87(17)	C32	C33	C28	120.2(5)
C22	P1	Au1A	119.91(17)	C31	C30	C29	120.3(5)
C2	P2	C8	103.3(2)	C26	C25	C24	120.5(5)
C2	P2	Au1[1]	113.02(16)	C5	C4	C3	120.1(6)
C8	P2	Au1[1]	109.39(16)	C28	C29	C30	119.4(5)
C1	P2	C2	106.3(2)	C32	C31	C30	120.3(5)
C1	P2	C8	105.2(2)	C21	C1	P2	127.8(3)
C1	P2	Au1[1]	118.34(17)	C10	C9	C8	118.9(6)
Au1A[1]	P2	C2	114.19(18)	C12	C13	C8	120.5(6)
Au1A[1]	P2	C8	110.23(17)	C11	C10	C9	121.3(6)
Au1A[1]	P2	C1	116.46(18)	F3S	C1S	S1S	115.0(7)
O1S	S1S	O3S	115.8(10)	F3S	C1S	F2S	105.9(8)

Table 11 Bond Angles for 3.

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
O1S	S1S	O2S	114.7(9)	F3S	C1S	F1S	109.4(9)
O1S	S1S	C1S	102.2(9)	F2S	C1S	S1S	112.1(7)
O3S	S1S	C1S	102.3(6)	F2S	C1S	F1S	105.7(9)
O2S	S1S	O3S	115.2(6)	F1S	C1S	S1S	108.3(7)
O2S	S1S	C1S	103.9(4)	P1	Au1	P2[1]	162.60(4)
C1	C21	P1	127.2(3)	P1	Au1	Au1[1]	107.13(4)
C2	C3	C4	120.5(5)	P2[1]	Au1	Au1[1]	85.52(3)
C33	C28	P1	118.2(4)	P1	Au1A	Au1A[1]	84.04(16)
C29	C28	P1	122.2(4)	P2[1]	Au1A	P1	163.03(11)
C29	C28	C33	119.6(5)	P2[1]	Au1A	Au1A[1]	107.71(17)
C3	C2	P2	120.0(4)	O1T	S1T	O3T	115.2(17)
C3	C2	C7	119.4(5)	O1T	S1T	C1T	103.2(12)
C7	C2	P2	120.5(4)	O3T	S1T	C1T	102.2(17)
C24	C23	C22	119.4(5)	O2T	S1T	O1T	115(2)
C9	C8	P2	123.4(4)	O2T	S1T	O3T	114(2)
C13	C8	P2	117.4(4)	O2T	S1T	C1T	105(2)
C13	C8	C9	119.2(5)	F3T	C1T	S1T	111.0(17)
C11	C12	C13	120.7(6)	F3T	C1T	F2T	107(2)
C23	C22	P1	121.2(4)	F3T	C1T	F1T	109(2)
C27	C22	P1	118.9(4)	F2T	C1T	S1T	110(2)
C27	C22	C23	119.8(5)	F2T	C1T	F1T	104(2)
C5	C6	C7	120.3(5)	F1T	C1T	S1T	114(2)

[1]1-X,-Y,1-Z

Table 12 Torsion Angles for 3.

A	B	C	D	Angle/°	A	B	C	D	Angle/°
P1	C21	C1	P2	2.3(7)	C11	C12	C13	C8	-0.4(10)
P1	C28	C33	C32	178.1(5)	C33	C28	C29	C30	2.6(8)
P1	C28	C29	C30	-178.0(4)	C33	C32	C31	C30	1.0(10)
P1	C22	C27	C26	174.4(4)	C4	C3	C2	P2	177.8(4)
P2	C2	C7	C6	-177.7(4)	C4	C3	C2	C7	-0.2(8)
P2	C8	C9	C10	178.3(5)	C29	C28	C33	C32	-2.5(9)
P2	C8	C13	C12	-178.1(5)	C29	C30	C31	C32	-0.9(9)
O1S	S1S	C1S	F3S	-176.7(12)	C31	C32	C33	C28	0.7(10)
O1S	S1S	C1S	F2S	62.2(11)	C31	C30	C29	C28	-0.9(8)
O1S	S1S	C1S	F1S	-54.0(12)	C1	P2	C2	C3	50.9(5)
C21	P1	C28	C33	-69.4(5)	C1	P2	C2	C7	-131.1(4)
C21	P1	C28	C29	111.2(4)	C1	P2	C8	C9	26.4(5)
C21	P1	C22	C23	-31.4(4)	C1	P2	C8	C13	-157.6(4)
C21	P1	C22	C27	152.4(4)	C9	C8	C13	C12	-1.9(9)
O3S	S1S	C1S	F3S	63.1(11)	C13	C8	C9	C10	2.4(9)

Table 12 Torsion Angles for 3.

A	B	C	D	Angle/°	A	B	C	D	Angle/°
O3S	S1S	C1S	F2S	-58.0(9)	C13	C12	C11	C10	2.2(10)
O3S	S1S	C1S	F1S	-174.2(9)	Au1	P1	C21	C1	44.9(5)
C3	C2	C7	C6	0.3(8)	Au1	P1	C28	C33	49.8(4)
C28	P1	C21	C1	159.9(5)	Au1	P1	C28	C29	-129.6(4)
C28	P1	C22	C23	78.2(4)	Au1	P1	C22	C23	-161.1(3)
C28	P1	C22	C27	-97.9(4)	Au1	P1	C22	C27	22.8(4)
O2S	S1S	C1S	F3S	-57.1(9)	Au1[1]	P2	C2	C3	-177.7(4)
O2S	S1S	C1S	F2S	-178.2(6)	Au1[1]	P2	C2	C7	0.3(4)
O2S	S1S	C1S	F1S	65.6(8)	Au1[1]	P2	C8	C9	-101.7(4)
C2	P2	C8	C9	137.7(5)	Au1[1]	P2	C8	C13	74.3(4)
C2	P2	C8	C13	-46.3(5)	Au1[1]	P2	C1	C21	-69.1(5)
C2	P2	C1	C21	59.3(5)	Au1A	P1	C21	C1	47.2(5)
C2	C3	C4	C5	0.1(9)	Au1A	P1	C28	C33	49.9(4)
C23	C22	C27	C26	-1.8(8)	Au1A	P1	C28	C29	-129.5(4)
C23	C24	C25	C26	-2.8(9)	Au1A	P1	C22	C23	-163.4(3)
C8	P2	C2	C3	-59.6(4)	Au1A	P1	C22	C27	20.4(4)
C8	P2	C2	C7	118.4(4)	Au1A[1]	P2	C2	C3	-179.3(4)
C8	P2	C1	C21	168.4(5)	Au1A[1]	P2	C2	C7	-1.3(5)
C8	C9	C10	C11	-0.6(10)	Au1A[1]	P2	C8	C9	-100.0(5)
C12	C11	C10	C9	-1.7(10)	Au1A[1]	P2	C8	C13	76.0(4)
C22	P1	C21	C1	-88.1(5)	Au1A[1]	P2	C1	C21	-69.2(5)
C22	P1	C28	C33	177.9(4)	O1T	S1T	C1T	F3T	-179.0(18)
C22	P1	C28	C29	-1.5(5)	O1T	S1T	C1T	F2T	62(2)
C22	C23	C24	C25	2.0(8)	O1T	S1T	C1T	F1T	-55(2)
C22	C27	C26	C25	1.0(9)	O3T	S1T	C1T	F3T	61(3)
C6	C5	C4	C3	-0.2(9)	O3T	S1T	C1T	F2T	-57(3)
C24	C23	C22	P1	-175.8(4)	O3T	S1T	C1T	F1T	-174(3)
C24	C23	C22	C27	0.3(7)	O2T	S1T	C1T	F3T	-59(3)
C5	C6	C7	C2	-0.3(9)	O2T	S1T	C1T	F2T	-177(3)
C27	C26	C25	C24	1.3(9)	O2T	S1T	C1T	F1T	66(3)
C7	C6	C5	C4	0.3(9)					

[1]1-X,-Y,1-Z

Table 13 Atomic Occupancy for 3.

Atom	*Occupancy*	Atom	*Occupancy*	Atom	*Occupancy*
S1S	0.729(6)	O1S	0.729(6)	O3S	0.729(6)
O2S	0.729(6)	F3S	0.729(6)	F2S	0.729(6)
F1S	0.729(6)	C1S	0.729(6)	Au1	0.8951(14)
Au1A	0.1049(14)	O1T	0.271(6)	S1T	0.271(6)
O3T	0.271(6)	O2T	0.271(6)	C1T	0.271(6)
F3T	0.271(6)	F2T	0.271(6)	F1T	0.271(6)

Crystal structure determination of [3]

Crystal Data for $C_{54}H_{44}Au_2F_6O_6P_4S_2$ (M =1484.82 g/mol): triclinic, space group P-1 (no. 2), a = 10.8708(5) Å, b = 11.0738(5) Å, c = 11.7702(5) Å, α = 76.6130(13)°, β = 83.5313(14)°, γ = 74.0031(14)°, V = 1323.22(10) Å^3, Z = 1, T = 180 K, μ(MoKα) = 5.808 mm^{-1}, *Dcalc* = 1.863 g/cm^3, 50095 reflections measured (3.562° ≤ 2Θ ≤ 59.392°), 7504 unique (R_{int} = 0.0681, R_{sigma} = 0.0460) which were used in all calculations. The final R_1 was 0.0386 (I > 2σ(I)) and wR_2 was 0.0745 (all data).

Refinement model description

Number of restraints - 125, number of constraints - 0.

Details:

```
1. Fixed Uiso
 At 1.2 times of:
  All C(H) groups
2. Restrained distances
 S1S-O1S ≈ S1T-O1T
 with sigma of 0.02
 S1S-O3S ≈ S1T-O3T
 with sigma of 0.02
 S1S-O2S ≈ S1T-O2T
 with sigma of 0.02
 S1S-C1S ≈ S1T-C1T
 with sigma of 0.02
 F3S-C1S ≈ F3T-C1T
 with sigma of 0.02
 F2S-C1S ≈ F2T-C1T
 with sigma of 0.02
 F1S-C1S ≈ F1T-C1T
 with sigma of 0.02
 S1S-F3S ≈ S1T-F3T
 with sigma of 0.04
 S1S-F2S ≈ S1T-F2T
 with sigma of 0.04
 S1S-F1S ≈ S1T-F1T
 with sigma of 0.04
 O1S-O3S ≈ O1T-O3T
 with sigma of 0.04
 O1S-O2S ≈ O1T-O2T
 with sigma of 0.04
 O1S-C1S ≈ O1T-C1T
 with sigma of 0.04
 O3S-O2S ≈ O3T-O2T
 with sigma of 0.04
 O3S-C1S ≈ O3T-C1T
 with sigma of 0.04
 O2S-C1S ≈ O2T-C1T
 with sigma of 0.04
 F3S-F2S ≈ F3T-F2T
 with sigma of 0.04
 F3S-F1S ≈ F3T-F1T
 with sigma of 0.04
 F2S-F1S ≈ F2T-F1T
 with sigma of 0.04
3. Uiso/Uaniso restraints and constraints
Uanis(Au1A) = Uanis(Au1)
4. Rigid body (RIGU) restrains
 S1S, O1S, O3S, O2S, F3S, F2S, F1S, C1S
 with sigma for 1-2 distances of 0.004 and sigma for 1-3 distances of 0.004
 S1T, O1T, O3T, O2T, F3T, F2T, F1T, C1T
 with sigma for 1-2 distances of 0.004 and sigma for 1-3 distances of 0.004
5. Others
 Sof(Au1A)=1-FVAR(1)
 Sof(Au1)=FVAR(1)
 Sof(O1T)=Sof(S1T)=Sof(O3T)=Sof(O2T)=Sof(C1T)=Sof(F3T)=Sof(F2T)=Sof(F1T)=1-
 FVAR(2)
 Sof(S1S)=Sof(O1S)=Sof(O3S)=Sof(O2S)=Sof(F3S)=Sof(F2S)=Sof(F1S)=Sof(C1S)=FVAR(2)
6.a Aromatic/amide H refined with riding coordinates:
 C21(H21), C3(H3), C23(H23), C12(H12), C6(H6), C32(H32), C24(H24), C5(H5),
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C27(H27), C26(H26), C7(H7), C11(H11), C33(H33), C30(H30), C25(H25), C4(H4), C29(H29), C31(H31), C1(H1), C9(H9), C13(H13), C10(H10)

Compound 1-BF_4

Table 14 Crystal data and structure refinement for 1-BF_4.

Identification code	**1-BF_4**
Empirical formula	$C_{52}H_{44}AuBF_4P_4$
Formula weight	1076.53
Temperature/K	180
Crystal system	triclinic
Space group	P-1
a/Å	11.5335(3)
b/Å	12.0756(3)
c/Å	16.8745(4)
α/°	97.9300(10)
β/°	92.0930(10)
γ/°	95.6690(10)
Volume/$Å^3$	2313.32(10)
Z	2
$\rho_{calc}g/cm^3$	1.545
μ/mm^{-1}	3.370
F(000)	1072.0
Crystal size/mm^3	0.2 × 0.2 × 0.15
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	3.554 to 56.564
Index ranges	$-15 \leq h \leq 15$, $-16 \leq k \leq 16$, $-22 \leq l \leq 22$
Reflections collected	99963
Independent reflections	11469 [R_{int} = 0.0282, R_{sigma} = 0.0145]
Data/restraints/parameters	11469/3/587
Goodness-of-fit on F^2	1.046
Final R indexes [I>=2σ (I)]	R_1 = 0.0149, wR_2 = 0.0372
Final R indexes [all data]	R_1 = 0.0165, wR_2 = 0.0379
Largest diff. peak/hole / e $Å^{-3}$	0.60/-0.35

Table 15 Bond Lengths for 1-BF_4.

Atom	Atom	Length/Å	Atom	Atom	Length/Å
Au01	P002	2.3951(4)	C00M	C00X	1.383(3)
Au01	P003	2.3996(4)	C00N	C016	1.389(3)
Au01	P004	2.3859(4)	C00O	C015	1.388(3)
Au01	P005	2.3976(4)	C00Q	C014	1.388(3)
P002	C007	1.8187(17)	C00Q	C01G	1.388(3)
P002	C00E	1.8225(16)	C00R	C01C	1.391(3)
P002	C00F	1.8089(16)	C00S	C00U	1.381(3)
P003	C00A	1.8143(16)	C00S	C01D	1.392(3)

Table 15 Bond Lengths for 1-BF_4.

Atom	Atom	Length/Å	Atom	Atom	Length/Å
P003	C00D	1.8152(17)	C00T	C01B	1.386(3)
P003	C00G	1.8252(16)	C00U	C011	1.394(2)
P004	C008	1.8144(16)	C00V	C01A	1.390(3)
P004	C009	1.8190(15)	C00W	C012	1.367(3)
P004	C00I	1.8142(16)	C00Y	C01H	1.387(3)
P005	C00C	1.8182(17)	C00Z	C019	1.393(3)
P005	C00Q	1.8142(17)	C010	C01E	1.395(3)
P005	C00U	1.8226(17)	C011	C017	1.386(3)
F006	B01P	1.332(14)	C012	C01A	1.369(3)
C007	C00C	1.330(2)	C013	C01J	1.377(3)
C008	C00D	1.332(2)	C013	C01K	1.367(3)
C009	C00H	1.389(2)	C014	C01K	1.391(3)
C009	C00K	1.400(2)	C015	C01O	1.375(3)
C00A	C00L	1.393(2)	C016	C01M	1.371(4)
C00A	C00V	1.381(2)	C017	C01F	1.373(3)
F00B	B01P	1.382(3)	F018	B01P	1.471(8)
C00E	C00J	1.384(3)	C019	C01M	1.368(4)
C00E	C010	1.390(3)	C01B	C01O	1.380(3)
C00F	C00O	1.400(2)	C01C	C01I	1.369(3)
C00F	C00T	1.385(3)	C01D	C01F	1.369(3)
C00G	C00R	1.389(2)	C01E	C01N	1.368(4)
C00G	C00Y	1.383(3)	C01G	C01J	1.386(3)
C00H	C00P	1.393(2)	C01H	C01I	1.367(3)
C00I	C00N	1.386(2)	C01L	C01N	1.367(4)
C00I	C00Z	1.393(2)	B01P	F01Q	1.326(7)
C00J	C01L	1.391(3)	B01P	F01R	1.364(6)
C00K	C00X	1.385(2)	B01P	F0	1.413(8)
C00L	C00W	1.391(3)	B01P	F1	1.359(5)
C00M	C00P	1.373(3)			

Table 16 Bond Angles for 1-BF_4.

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
P002	Au01	P003	127.294(13)	C00W	C00L	C00A	119.59(18)
P002	Au01	P005	85.372(14)	C00P	C00M	C00X	120.40(16)
P004	Au01	P002	120.756(13)	C00I	C00N	C016	119.7(2)
P004	Au01	P003	85.954(13)	C015	C00O	C00F	119.79(19)
P004	Au01	P005	127.556(14)	C00M	C00P	C00H	119.87(17)
P005	Au01	P003	114.867(14)	C014	C00Q	P005	119.72(14)
C007	P002	Au01	104.18(6)	C01G	C00Q	P005	121.06(14)
C007	P002	C00E	98.88(8)	C01G	C00Q	C014	119.03(17)
C00E	P002	Au01	117.61(6)	C00G	C00R	C01C	120.40(19)

Table 16 Bond Angles for 1-BF_4.

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
C00F	P002	Au01	123.77(5)	C00U	C00S	C01D	120.86(18)
C00F	P002	C007	104.18(8)	C00F	C00T	C01B	120.25(19)
C00F	P002	C00E	104.50(8)	C00S	C00U	P005	118.96(13)
C00A	P003	Au01	120.37(5)	C00S	C00U	C011	118.47(16)
C00A	P003	C00D	104.27(8)	C011	C00U	P005	122.54(14)
C00A	P003	C00G	103.44(7)	C00A	C00V	C01A	120.62(18)
C00D	P003	Au01	104.22(5)	C012	C00W	C00L	120.72(18)
C00D	P003	C00G	101.74(7)	C00M	C00X	C00K	120.29(17)
C00G	P003	Au01	120.18(5)	C00G	C00Y	C01H	120.43(19)
C008	P004	Au01	104.68(5)	C019	C00Z	C00I	120.48(19)
C008	P004	C009	101.45(7)	C00E	C010	C01E	119.4(2)
C009	P004	Au01	119.79(5)	C017	C011	C00U	120.30(18)
C00I	P004	Au01	120.18(5)	C00W	C012	C01A	120.06(18)
C00I	P004	C008	104.61(8)	C01K	C013	C01J	119.98(19)
C00I	P004	C009	103.59(7)	C00Q	C014	C01K	119.8(2)
C00C	P005	Au01	104.15(5)	C01O	C015	C00O	120.2(2)
C00C	P005	C00U	103.21(8)	C01M	C016	C00N	120.6(2)
C00Q	P005	Au01	119.25(5)	C01F	C017	C011	120.28(18)
C00Q	P005	C00C	101.74(8)	C01M	C019	C00Z	119.6(2)
C00Q	P005	C00U	104.57(8)	C012	C01A	C00V	120.0(2)
C00U	P005	Au01	121.02(6)	C01O	C01B	C00T	120.0(2)
C00C	C007	P002	121.52(13)	C01I	C01C	C00R	120.4(2)
C00D	C008	P004	121.79(12)	C01F	C01D	C00S	119.9(2)
C00H	C009	P004	120.02(12)	C01N	C01E	C010	120.3(2)
C00H	C009	C00K	119.26(15)	C01D	C01F	C017	120.17(18)
C00K	C009	P004	120.68(12)	C01J	C01G	C00Q	120.4(2)
C00L	C00A	P003	122.48(13)	C01I	C01H	C00Y	120.7(2)
C00V	C00A	P003	118.51(13)	C01H	C01I	C01C	119.57(18)
C00V	C00A	C00L	118.99(16)	C013	C01J	C01G	120.1(2)
C007	C00C	P005	122.12(13)	C013	C01K	C014	120.7(2)
C008	C00D	P003	122.39(12)	C01N	C01L	C00J	119.7(2)
C00J	C00E	P002	119.09(13)	C019	C01M	C016	120.50(19)
C00J	C00E	C010	119.44(17)	C01L	C01N	C01E	120.73(19)
C010	C00E	P002	121.22(15)	C015	C01O	C01B	120.38(19)
C00O	C00F	P002	120.29(13)	F006	B01P	F00B	118.7(9)
C00T	C00F	P002	120.20(14)	F006	B01P	F018	95.9(9)
C00T	C00F	C00O	119.38(16)	F00B	B01P	F018	89.5(8)
C00R	C00G	P003	121.47(13)	F00B	B01P	F0	107.3(4)
C00Y	C00G	P003	119.97(13)	F01Q	B01P	F006	118.2(9)
C00Y	C00G	C00R	118.47(16)	F01Q	B01P	F00B	119.9(5)
C009	C00H	C00P	120.35(17)	F01Q	B01P	F018	102.7(6)
C00N	C00I	P004	121.68(14)	F01R	B01P	F00B	111.0(4)
C00N	C00I	C00Z	119.05(16)	F01R	B01P	F0	114.5(5)

Table 16 Bond Angles for 1-BF_4.

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
C00Z	C00I	P004	118.95(13)	F1	B01P	F00B	106.0(3)
C00E	C00J	C01L	120.4(2)	F1	B01P	F01R	112.9(3)
C00X	C00K	C009	119.82(16)	F1	B01P	F0	104.5(5)

Table 17 Torsion Angles for 1-BF_4.

A	B	C	D	Angle/°	A	B	C	D	Angle/°
Au01	P002	C007	C00C	14.00(15)	C00E	P002	C007	C00C	-107.55(15)
Au01	P002	C00E	C00J	-9.70(16)	C00E	P002	C00F	C00O	44.87(15)
Au01	P002	C00E	C010	176.11(13)	C00E	P002	C00F	C00T	-139.32(14)
Au01	P002	C00F	C00O	-93.61(14)	C00E	C00J	C01L	C01N	-0.5(3)
Au01	P002	C00F	C00T	82.20(15)	C00E	C010	C01E	C01N	-0.3(3)
Au01	P003	C00A	C00L	154.07(12)	C00F	P002	C007	C00C	144.94(14)
Au01	P003	C00A	C00V	-27.76(16)	C00F	P002	C00E	C00J	-151.25(14)
Au01	P003	C00D	C008	-3.81(16)	C00F	P002	C00E	C010	34.56(17)
Au01	P003	C00G	C00R	111.80(14)	C00F	C00O	C015	C01O	-0.1(3)
Au01	P003	C00G	C00Y	-64.73(16)	C00F	C00T	C01B	C01O	0.2(3)
Au01	P004	C008	C00D	9.41(15)	C00G	P003	C00A	C00L	-68.28(16)
Au01	P004	C009	C00H	14.33(15)	C00G	P003	C00A	C00V	109.89(15)
Au01	P004	C009	C00K	-163.37(11)	C00G	P003	C00D	C008	-129.43(15)
Au01	P004	C00I	C00N	84.80(16)	C00G	C00R	C01C	C01I	0.2(3)
Au01	P004	C00I	C00Z	-88.57(14)	C00G	C00Y	C01H	C01I	-0.8(4)
Au01	P005	C00C	C007	-8.81(16)	C00H	C009	C00K	C00X	0.4(2)
Au01	P005	C00Q	C014	-71.35(16)	C00I	P004	C008	C00D	136.67(14)
Au01	P005	C00Q	C01G	103.67(15)	C00I	P004	C009	C00H	-122.93(13)
Au01	P005	C00U	C00S	-1.66(18)	C00I	P004	C009	C00K	59.37(14)
Au01	P005	C00U	C011	176.32(13)	C00I	C00N	C016	C01M	1.0(3)
P002	C007	C00C	P005	-3.6(2)	C00I	C00Z	C019	C01M	0.1(3)
P002	C00E	C00J	C01L	-173.80(16)	C00J	C00E	C010	C01E	-0.1(3)
P002	C00E	C010	C01E	174.06(17)	C00J	C01L	C01N	C01E	0.0(3)
P002	C00F	C00O	C015	176.46(15)	C00K	C009	C00H	C00P	-0.8(2)
P002	C00F	C00T	C01B	-176.52(15)	C00L	C00A	C00V	C01A	1.3(3)
P003	C00A	C00L	C00W	178.35(14)	C00L	C00W	C012	C01A	0.6(3)
P003	C00A	C00V	C01A	-176.94(17)	C00N	C00I	C00Z	C019	0.1(3)
P003	C00G	C00R	C01C	-176.94(15)	C00N	C016	C01M	C019	-0.8(4)
P003	C00G	C00Y	C01H	177.27(17)	C00O	C00F	C00T	C01B	-0.7(3)
P004	C008	C00D	P003	-3.9(2)	C00O	C015	C01O	C01B	-0.4(3)
P004	C009	C00H	C00P	-178.58(13)	C00P	C00M	C00X	C00K	-0.7(3)
P004	C009	C00K	C00X	178.14(13)	C00Q	P005	C00C	C007	-133.35(15)
P004	C00I	C00N	C016	-174.00(17)	C00Q	P005	C00U	C00S	136.53(16)
P004	C00I	C00Z	C019	173.62(14)	C00Q	P005	C00U	C011	-45.48(17)
P005	C00Q	C014	C01K	175.77(15)	C00Q	C014	C01K	C013	-0.5(3)
P005	C00Q	C01G	C01J	-175.41(16)	C00Q	C01G	C01J	C013	-0.1(3)
P005	C00U	C011	C017	179.86(15)	C00R	C00G	C00Y	C01H	0.6(3)
C007	P002	C00E	C00J	101.50(15)	C00R	C01C	C01I	C01H	-0.3(3)
C007	P002	C00E	C010	-72.69(16)	C00S	C00U	C011	C017	-2.1(3)
C007	P002	C00F	C00O	148.15(14)	C00S	C01D	C01F	C017	-2.1(4)
C007	P002	C00F	C00T	-36.03(15)	C00T	C00F	C00O	C015	0.6(3)
C008	P004	C009	C00H	128.78(13)	C00T	C01B	C01O	C015	0.3(3)

Table 17 Torsion Angles for 1-BF_4.

A	B	C	D	Angle/°	A	B	C	D	Angle/°
C008	P004	C009	C00K	-48.91(14)	C00U	P005	C00C	C007	118.43(15)
C008	P004	C00I	C00N	-32.24(17)	C00U	P005	C00Q	C014	149.55(15)
C008	P004	C00I	C00Z	154.39(13)	C00U	P005	C00Q	C01G	-35.44(17)
C009	P004	C008	C00D	-115.85(15)	C00U	C00S	C01D	C01F	1.0(4)
C009	P004	C00I	C00N	-138.15(15)	C00U	C011	C017	C01F	1.0(3)
C009	P004	C00I	C00Z	48.48(15)	C00V	C00A	C00L	C00W	0.2(3)
C009	C00H	C00P	C00M	0.5(3)	C00W	C012	C01A	C00V	0.9(4)
C009	C00K	C00X	C00M	0.4(3)	C00X	C00M	C00P	C00H	0.3(3)
C00A	P003	C00D	C008	123.25(15)	C00Y	C00G	C00R	C01C	-0.4(3)
C00A	P003	C00G	C00R	-25.95(16)	C00Y	C01H	C01I	C01C	0.6(3)
C00A	P003	C00G	C00Y	157.52(15)	C00Z	C00I	C00N	C016	-0.6(3)
C00A	C00L	C00W	C012	-1.1(3)	C00Z	C019	C01M	C016	0.3(3)
C00A	C00V	C01A	C012	-1.9(4)	C010	C00E	C00J	C01L	0.5(3)
C00C	P005	C00Q	C014	42.38(16)	C010	C01E	C01N	C01L	0.3(4)
C00C	P005	C00Q	C01G	-142.60(15)	C011	C017	C01F	C01D	1.1(3)
C00C	P005	C00U	C00S	-117.39(16)	C014	C00Q	C01G	C01J	-0.4(3)
C00C	P005	C00U	C011	60.59(16)	C01D	C00S	C00U	P005	179.21(19)
C00D	P003	C00A	C00L	37.78(16)	C01D	C00S	C00U	C011	1.1(3)
C00D	P003	C00A	C00V	-144.05(15)	C01G	C00Q	C014	C01K	0.6(3)
C00D	P003	C00G	C00R	-133.92(15)	C01J	C013	C01K	C014	0.0(3)
C00D	P003	C00G	C00Y	49.55(17)	C01K	C013	C01J	C01G	0.3(3)

Table 18 Atomic Occupancy for 1.BF_4.

Atom	*Occupancy*	Atom	*Occupancy*	Atom	*Occupancy*
F006	0.342(18)	F018	0.342(18)	F01Q	0.342(18)
F01R	0.658(18)	F0	0.658(18)	F1	0.658(18)

Crystal structure determination of [1.BF_4]

Crystal Data for $C_{52}H_{44}AuBF_4P_4$ (M =1076.53 g/mol): triclinic, space group P-1 (no. 2), a = 11.5335(3) Å, b = 12.0756(3) Å, c = 16.8745(4) Å, α = 97.9300(10)°, β = 92.0930(10)°, γ = 95.6690(10)°, V = 2313.32(10) Å^3, Z = 2, T = 180 K, μ(MoKα) = 3.370 mm^{-1}, *Dcalc* = 1.545 g/cm^3, 99963 reflections measured (3.554° ≤ 2Θ ≤ 56.564°), 11469 unique (R_{int} = 0.0282, R_{sigma} = 0.0145) which were used in all calculations. The final R_1 was 0.0149 (I > 2σ(I)) and wR_2 was 0.0379 (all data).

Refinement model description

Number of restraints - 3, number of constraints - unknown.

Details:

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1. Fixed Uiso
 At 1.2 times of:
  All C(H) groups
2. Restrained distances
 F006-B01P ≈ F1-B01P
 with sigma of 0.02
 F018-B01P ≈ F0-B01P
 with sigma of 0.02
 B01P-F01Q ≈ B01P-F01R
 with sigma of 0.02
3. Others
 Sof(F01R)=Sof(F0)=Sof(F1)=1-FVAR(1)
 Sof(F006)=Sof(F018)=Sof(F01Q)=FVAR(1)
4.a Aromatic/amide H refined with riding coordinates:
 C007(H007), C008(H008), C00C(H00C), C00D(H00D), C00H(H00H), C00J(H00J),
 C00K(H00K), C00L(H00L), C00M(H00M), C00N(H00N), C00O(H00O), C00P(H00P),
 C00R(H00R), C00S(H00S), C00T(H00T), C00V(H00V), C00W(H00W), C00X(H00X),
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C00Y(H00Y), C00Z(H00Z), C010(H010), C011(H011), C012(H012), C013(H013),
C014(H014), C015(H015), C016(H016), C017(H017), C019(H019), C01A(H01A),
C01B(H01B), C01C(H01C), C01D(H01D), C01E(H01E), C01F(H01F), C01G(H01G),
C01H(H01H), C01I(H01I), C01J(H01J), C01K(H01K), C01L(H01L), C01M(H01M),
C01N(H01N), C01O(H01O)
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Compound 1-PF_6

Table 19 Crystal data and structure refinement for 1-PF_6.

Identification code	**1-PF_6**
Empirical formula	$C_{56}H_{52}AuF_6OP_5$
Formula weight	1206.79
Temperature/K	180
Crystal system	orthorhombic
Space group	$P2_12_12_1$
a/Å	14.5642(12)
b/Å	16.7939(14)
c/Å	20.9855(18)
α/°	90
β/°	90
γ/°	90
Volume/$Å^3$	5132.8(7)
Z	4
$\rho_{calc}g/cm^3$	1.562
μ/mm^{-1}	3.084
F(000)	2416.0
Crystal size/mm^3	0.23 × 0.2 × 0.18
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	3.106 to 56.68
Index ranges	$-19 \leq h \leq 19$, $-22 \leq k \leq 22$, $-28 \leq l \leq 28$
Reflections collected	158673
Independent reflections	12804 [R_{int} = 0.0550, R_{sigma} = 0.0365]
Data/restraints/parameters	12804/75/622
Goodness-of-fit on F^2	1.025
Final R indexes [I>=2σ (I)]	R_1 = 0.0244, wR_2 = 0.0522
Final R indexes [all data]	R_1 = 0.0307, wR_2 = 0.0545
Largest diff. peak/hole / e $Å^{-3}$	0.92/-0.65
Flack parameter	-0.0029(19)

Table 20 Bond Lengths for 1-PF_6.

Atom	Atom	Length/Å	Atom	Atom	Length/Å
Au01	P002	2.3781(11)	C00M	C010	1.403(6)
Au01	P003	2.3673(10)	C00O	C011	1.364(8)

Table 20 Bond Lengths for 1-PF_6.

Atom	Atom	Length/Å	Atom	Atom	Length/Å
Au01	P004	2.3775(11)	C00R	C00S	1.344(8)
Au01	P005	2.3703(11)	C00R	C010	1.380(8)
P002	C007	1.824(5)	C00T	C01I	1.377(8)
P002	C00L	1.808(4)	C00T	C01O	1.362(9)
P002	C01K	1.818(5)	C00U	C012	1.354(8)
P003	C008	1.819(4)	C00U	C01Q	1.364(9)
P003	C00W	1.822(4)	C00W	C00Y	1.383(7)
P003	C018	1.813(4)	C00W	C01A	1.378(7)
P004	C00G	1.817(4)	C00X	C017	1.388(7)
P004	C00J	1.821(4)	C00X	C01S	1.376(7)
P004	C00X	1.809(5)	C00Y	C016	1.395(7)
P005	C00E	1.825(4)	C00Z	C012	1.386(7)
P005	C00I	1.824(4)	C011	C01G	1.361(8)
P005	C00Q	1.812(5)	C013	C015	1.374(6)
P006	F009	1.578(4)	C014	C01Q	1.379(7)
P006	F00A	1.568(4)	C016	C01F	1.365(9)
P006	F00D	1.567(4)	C017	C01E	1.388(7)
P006	F00K	1.564(4)	C019	C01K	1.388(7)
P006	F00N	1.551(4)	C019	C01M	1.373(7)
P006	F00V	1.565(4)	C01A	C01J	1.382(7)
C007	C01B	1.379(7)	C01B	C01I	1.383(7)
C007	C01N	1.390(7)	C01D	C01M	1.389(10)
C008	C00P	1.391(6)	C01D	C01T	1.342(9)
C008	C015	1.382(6)	C01E	C01H	1.371(9)
C00B	C00I	1.372(6)	C01F	C01J	1.372(9)
C00B	C00O	1.390(7)	C01G	C01U	1.387(7)
C00C	C00H	1.367(8)	C01H	C01P	1.345(9)
C00C	C00P	1.388(7)	C01K	C01R	1.373(8)
C00E	C00F	1.383(7)	C01N	C01O	1.394(8)
C00E	C00M	1.385(6)	C01P	C01S	1.387(8)
C00F	C00S	1.369(7)	C01R	C01T	1.393(8)
C00G	C00Q	1.321(6)	O2	C3	1.592(11)
C00H	C013	1.371(7)	O2	C6	1.588(13)
C00I	C01U	1.381(7)	C3	C4	1.433(10)
C00J	C00Z	1.381(7)	C4	C5	1.364(11)
C00J	C014	1.386(6)	C5	C6	1.221(12)
C00L	C018	1.325(6)			

Table 21 Bond Angles for 1-PF_6.

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
P003	Au01	P002	86.84(4)	C00B	C00I	P005	122.3(4)

Table 21 Bond Angles for 1-PF_6.

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
P003	Au01	P004	111.47(4)	C00B	C00I	C01U	118.4(4)
P003	Au01	P005	134.91(4)	C01U	C00I	P005	119.0(4)
P004	Au01	P002	132.35(4)	C00Z	C00J	P004	123.0(4)
P005	Au01	P002	111.35(4)	C00Z	C00J	C014	119.3(4)
P005	Au01	P004	86.82(4)	C014	C00J	P004	117.7(4)
C007	P002	Au01	115.71(16)	C018	C00L	P002	122.3(4)
C00L	P002	Au01	104.19(14)	C00E	C00M	C010	119.4(5)
C00L	P002	C007	101.6(2)	C011	C00O	C00B	119.7(5)
C00L	P002	C01K	105.0(2)	C00C	C00P	C008	119.7(5)
C01K	P002	Au01	123.01(17)	C00G	C00Q	P005	122.7(3)
C01K	P002	C007	104.8(2)	C00S	C00R	C010	121.3(5)
C008	P003	Au01	113.70(15)	C00R	C00S	C00F	119.9(5)
C008	P003	C00W	104.78(19)	C01O	C00T	C01I	120.0(6)
C00W	P003	Au01	124.23(17)	C012	C00U	C01Q	119.4(5)
C018	P003	Au01	104.25(14)	C00Y	C00W	P003	117.9(4)
C018	P003	C008	102.1(2)	C01A	C00W	P003	123.1(4)
C018	P003	C00W	105.3(2)	C01A	C00W	C00Y	119.0(4)
C00G	P004	Au01	103.87(15)	C017	C00X	P004	122.3(4)
C00G	P004	C00J	101.9(2)	C01S	C00X	P004	119.1(4)
C00J	P004	Au01	116.66(15)	C01S	C00X	C017	118.5(5)
C00X	P004	Au01	123.09(16)	C00W	C00Y	C016	120.1(5)
C00X	P004	C00G	104.6(2)	C00J	C00Z	C012	119.4(5)
C00X	P004	C00J	104.1(2)	C00R	C010	C00M	119.2(5)
C00E	P005	Au01	126.12(15)	C01G	C011	C00O	120.1(5)
C00I	P005	Au01	113.49(15)	C00U	C012	C00Z	121.3(5)
C00I	P005	C00E	104.1(2)	C00H	C013	C015	120.0(5)
C00Q	P005	Au01	103.97(15)	C01Q	C014	C00J	119.7(5)
C00Q	P005	C00E	103.4(2)	C013	C015	C008	120.9(4)
C00Q	P005	C00I	103.1(2)	C01F	C016	C00Y	120.0(6)
F00A	P006	F009	89.5(2)	C01E	C017	C00X	120.2(6)
F00D	P006	F009	89.9(2)	C00L	C018	P003	122.4(4)
F00D	P006	F00A	178.9(3)	C01M	C019	C01K	120.6(6)
F00K	P006	F009	91.8(3)	C00W	C01A	C01J	120.6(5)
F00K	P006	F00A	90.9(3)	C007	C01B	C01I	121.1(5)
F00K	P006	F00D	88.3(3)	C01T	C01D	C01M	119.9(6)
F00K	P006	F00V	89.0(3)	C01H	C01E	C017	119.8(6)
F00N	P006	F009	89.6(3)	C016	C01F	C01J	120.1(5)
F00N	P006	F00A	89.2(3)	C011	C01G	C01U	120.3(5)
F00N	P006	F00D	91.6(3)	C01P	C01H	C01E	120.5(6)
F00N	P006	F00K	178.6(3)	C00T	C01I	C01B	119.8(6)
F00N	P006	F00V	89.6(3)	C01F	C01J	C01A	120.2(6)
F00V	P006	F009	178.2(3)	C019	C01K	P002	123.2(4)
F00V	P006	F00A	92.1(3)	C01R	C01K	P002	118.0(4)

Table 21 Bond Angles for 1-PF_6.

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
F00V	P006	F00D	88.6(3)	C01R	C01K	C019	118.8(5)
C01B	C007	P002	118.7(4)	C019	C01M	C01D	119.8(6)
C01B	C007	C01N	118.5(5)	C007	C01N	C01O	120.1(5)
C01N	C007	P002	122.7(4)	C00T	C01O	C01N	120.4(5)
C00P	C008	P003	122.4(4)	C01H	C01P	C01S	120.4(7)
C015	C008	P003	118.6(3)	C00U	C01Q	C014	121.0(5)
C015	C008	C00P	118.8(4)	C01K	C01R	C01T	120.1(6)
C00I	C00B	C00O	121.0(5)	C00X	C01S	C01P	120.5(6)
C00H	C00C	C00P	120.4(5)	C01D	C01T	C01R	120.9(6)
C00F	C00E	P005	122.1(4)	C00I	C01U	C01G	120.4(5)
C00F	C00E	C00M	119.0(4)	C6	O2	C3	99.8(8)
C00M	C00E	P005	118.9(3)	C4	C3	O2	98.2(7)
C00S	C00F	C00E	121.2(5)	C5	C4	C3	113.8(9)
C00Q	C00G	P004	122.0(3)	C6	C5	C4	109.4(12)
C00C	C00H	C013	120.1(5)	C5	C6	O2	104.8(13)

Table 22 Torsion Angles for 1-PF_6.

A	B	C	D	Angle/°	A	B	C	D	Angle/°
Au01	P002	C007	C01B	54.8(4)	C00J	C00Z	C012	C00U	0.3(9)
Au01	P002	C007	C01N	-121.3(4)	C00J	C014	C01Q	C00U	-0.1(9)
Au01	P002	C00L	C018	0.2(6)	C00L	P002	C007	C01B	-57.3(4)
Au01	P002	C01K	C019	-142.3(4)	C00L	P002	C007	C01N	126.6(4)
Au01	P002	C01K	C01R	38.7(5)	C00L	P002	C01K	C019	-23.9(5)
Au01	P003	C008	C00P	-120.0(4)	C00L	P002	C01K	C01R	157.1(5)
Au01	P003	C008	C015	55.7(4)	C00M	C00E	C00F	C00S	-0.8(7)
Au01	P003	C00W	C00Y	29.0(4)	C00O	C00B	C00I	P005	173.8(4)
Au01	P003	C00W	C01A	-152.0(3)	C00O	C00B	C00I	C01U	0.2(8)
Au01	P003	C018	C00L	-2.5(6)	C00O	C011	C01G	C01U	2.9(11)
Au01	P004	C00G	C00Q	6.3(4)	C00P	C008	C015	C013	-0.5(8)
Au01	P004	C00J	C00Z	-130.6(4)	C00P	C00C	C00H	C013	-0.4(9)
Au01	P004	C00J	C014	47.8(4)	C00Q	P005	C00E	C00F	-46.4(4)
Au01	P004	C00X	C017	-144.1(4)	C00Q	P005	C00E	C00M	131.8(4)
Au01	P004	C00X	C01S	36.7(6)	C00Q	P005	C00I	C00B	141.6(4)
Au01	P005	C00E	C00F	-165.1(3)	C00Q	P005	C00I	C01U	-44.8(5)
Au01	P005	C00E	C00M	13.1(4)	C00S	C00R	C010	C00M	1.9(8)
Au01	P005	C00I	C00B	-106.6(4)	C00W	P003	C008	C00P	18.7(5)
Au01	P005	C00I	C01U	67.0(5)	C00W	P003	C008	C015	-165.6(4)
Au01	P005	C00Q	C00G	-5.3(4)	C00W	P003	C018	C00L	-134.7(6)
P002	C007	C01B	C01I	-176.1(4)	C00W	C00Y	C016	C01F	0.1(9)
P002	C007	C01N	C01O	176.4(4)	C00W	C01A	C01J	C01F	0.4(9)
P002	C00L	C018	P003	1.6(8)	C00X	P004	C00G	C00Q	-123.9(4)

Table 22 Torsion Angles for 1-PF_6.

A	B	C	D	Angle/°	A	B	C	D	Angle/°
P002	C01K	C01R	C01T	178.7(6)	C00X	P004	C00J	C00Z	8.5(5)
P003	C008	C00P	C00C	175.7(4)	C00X	P004	C00J	C014	-173.1(4)
P003	C008	C015	C013	-176.4(5)	C00X	C017	C01E	C01H	2.2(9)
P003	C00W	C00Y	C016	178.4(4)	C00Y	C00W	C01A	C01J	0.5(8)
P003	C00W	C01A	C01J	-178.5(4)	C00Y	C016	C01F	C01J	0.8(9)
P004	C00G	C00Q	P005	-0.7(6)	C00Z	C00J	C014	C01Q	0.5(8)
P004	C00J	C00Z	C012	177.8(4)	C010	C00R	C00S	C00F	-1.5(8)
P004	C00J	C014	C01Q	-178.0(4)	C011	C01G	C01U	C00I	-1.8(11)
P004	C00X	C017	C01E	-179.6(4)	C012	C00U	C01Q	C014	-0.3(10)
P004	C00X	C01S	C01P	177.0(6)	C014	C00J	C00Z	C012	-0.6(8)
P005	C00E	C00F	C00S	177.4(4)	C015	C008	C00P	C00C	0.0(7)
P005	C00E	C00M	C010	-177.2(4)	C016	C01F	C01J	C01A	-1.1(9)
P005	C00I	C01U	C01G	-173.6(6)	C017	C00X	C01S	C01P	-2.3(10)
C007	P002	C00L	C018	120.8(6)	C017	C01E	C01H	C01P	-1.3(11)
C007	P002	C01K	C019	82.7(5)	C018	P003	C008	C00P	128.3(4)
C007	P002	C01K	C01R	-96.3(5)	C018	P003	C008	C015	-56.0(5)
C007	C01B	C01I	C00T	-0.6(9)	C018	P003	C00W	C00Y	148.6(4)
C007	C01N	C01O	C00T	-0.3(8)	C018	P003	C00W	C01A	-32.3(5)
C008	P003	C00W	C00Y	-104.1(4)	C019	C01K	C01R	C01T	-0.3(10)
C008	P003	C00W	C01A	75.0(4)	C01A	C00W	C00Y	C016	-0.7(8)
C008	P003	C018	C00L	116.1(6)	C01B	C007	C01N	C01O	0.4(8)
C00B	C00I	C01U	C01G	0.2(9)	C01E	C01H	C01P	C01S	-1.3(14)
C00B	C00O	C011	C01G	-2.5(10)	C01H	C01P	C01S	C00X	3.2(13)
C00C	C00H	C013	C015	-0.2(9)	C01I	C00T	C01O	C01N	-0.2(9)
C00E	P005	C00I	C00B	34.0(5)	C01K	P002	C007	C01B	-166.4(4)
C00E	P005	C00I	C01U	-152.5(5)	C01K	P002	C007	C01N	17.6(5)
C00E	P005	C00Q	C00G	-138.4(4)	C01K	P002	C00L	C018	-130.3(6)
C00E	C00F	C00S	C00R	1.0(8)	C01K	C019	C01M	C01D	0.1(8)
C00E	C00M	C010	C00R	-1.6(7)	C01K	C01R	C01T	C01D	-0.7(12)
C00F	C00E	C00M	C010	1.1(7)	C01M	C019	C01K	P002	-178.3(4)
C00G	P004	C00J	C00Z	117.0(4)	C01M	C019	C01K	C01R	0.6(8)
C00G	P004	C00J	C014	-64.5(4)	C01M	C01D	C01T	C01R	1.4(12)
C00G	P004	C00X	C017	-26.4(5)	C01N	C007	C01B	C01I	0.1(8)
C00G	P004	C00X	C01S	154.4(5)	C01O	C00T	C01I	C01B	0.7(9)
C00H	C00C	C00P	C008	0.5(8)	C01Q	C00U	C012	C00Z	0.2(10)
C00H	C013	C015	C008	0.6(9)	C01S	C00X	C017	C01E	-0.3(8)
C00I	P005	C00E	C00F	61.1(4)	C01T	C01D	C01M	C019	-1.1(10)
C00I	P005	C00E	C00M	-120.8(4)	O2	C3	C4	C5	-4.2(15)
C00I	P005	C00Q	C00G	113.3(4)	C3	O2	C6	C5	34(2)
C00I	C00B	C00O	C011	0.9(8)	C3	C4	C5	C6	29(2)
C00J	P004	C00G	C00Q	128.0(4)	C4	C5	C6	O2	-38(2)
C00J	P004	C00X	C017	80.2(5)	C6	O2	C3	C4	-15.3(14)
C00J	P004	C00X	C01S	-99.0(5)					

Crystal structure determination of [1-PF_6]

Crystal Data for $C_{56}H_{52}AuF_6OP_5$ (*M* =1206.79 g/mol): orthorhombic, space group $P2_12_12_1$ (no. 19), *a* = 14.5642(12) Å, *b* = 16.7939(14) Å, *c* = 20.9855(18) Å, *V* = 5132.8(7) Å^3, *Z* = 4, *T* = 180 K, μ(MoKα) = 3.084 mm^{-1}, *Dcalc* = 1.562 g/cm^3, 158673 reflections measured (3.106° ≤ 2Θ ≤ 56.68°), 12804 unique (R_{int} = 0.0550, R_{sigma} = 0.0365) which were used in all calculations. The final R_1 was 0.0244 (I > 2σ(I)) and wR_2 was 0.0545 (all data).

Refinement model description

Number of restraints - 75, number of constraints - unknown.

Details:

```
1. Fixed Uiso
 At 1.2 times of:
  All C(H) groups, All C(H,H) groups
2. Restrained distances
 O2-C3 = O2-C6
 1.44 with sigma of 0.02
 C3-C4 = C5-C6
 1.53 with sigma of 0.02
 C4-C5
 1.54 with sigma of 0.02
 O2-C4 = O2-C5 = C3-C5 = C4-C6
 2.38 with sigma of 0.04
 C3-C4 ≈ C4-C5 ≈ C5-C6
 with sigma of 0.02
 O2-C3 ≈ O2-C6
 with sigma of 0.02
 O2-C4 ≈ O2-C5
 with sigma of 0.04
 C4-C6 ≈ C3-C5
 with sigma of 0.04
3. Uiso/Uaniso restraints and constraints
O2 ≈ C3 ≈ C4 ≈ C5 ≈ C6: within 2A with sigma of 0.04 and sigma
for terminal atoms of 0.08 within 2A
4. Rigid body (RIGU) restrains
 O2, C3, C4, C5, C6
 with sigma for 1-2 distances of 0.004 and sigma for 1-3 distances of 0.004
 C6, C5
 with sigma for 1-2 distances of 0.01 and sigma for 1-3 distances of 0.01
5.a Secondary CH2 refined with riding coordinates:
 C3(H3A,H3B), C4(H4A,H4B), C5(H5A,H5B), C6(H6A,H6B)
5.b Aromatic/amide H refined with riding coordinates:
 C00B(H00B), C00C(H00C), C00F(H00F), C00G(H00G), C00H(H00H), C00L(H00L),
 C00M(H00M), C00O(H00O), C00P(H00P), C00Q(H00Q), C00R(H00R), C00S(H00S),
 C00T(H00T), C00U(H00U), C00Y(H00Y), C00Z(H00Z), C010(H010), C011(H011),
 C012(H012), C013(H013), C014(H014), C015(H015), C016(H016), C017(H017),
 C018(H018), C019(H019), C01A(H01A), C01B(H01B), C01D(H01D), C01E(H01E),
 C01F(H01F), C01G(H01G), C01H(H01H), C01I(H01I), C01J(H01J), C01M(H01M),
 C01N(H01N), C01O(H01O), C01P(H01P), C01Q(H01Q), C01R(H01R), C01S(H01S),
 C01T(H01T), C01U(H01U)
```

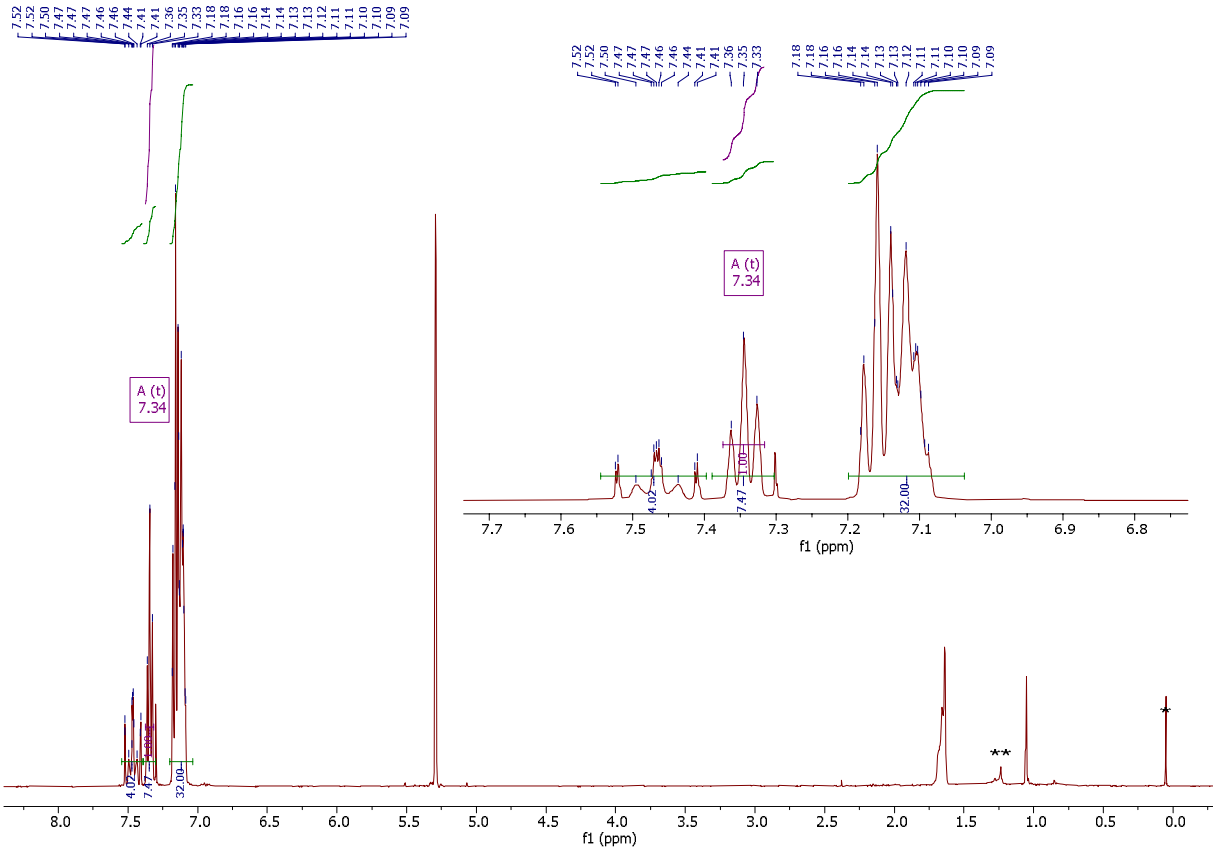

*Figure S 3: ^{1}H NMR (CD_2Cl_2, 298 K) spectrum of 1-Cl. * silicon grease ** grease*

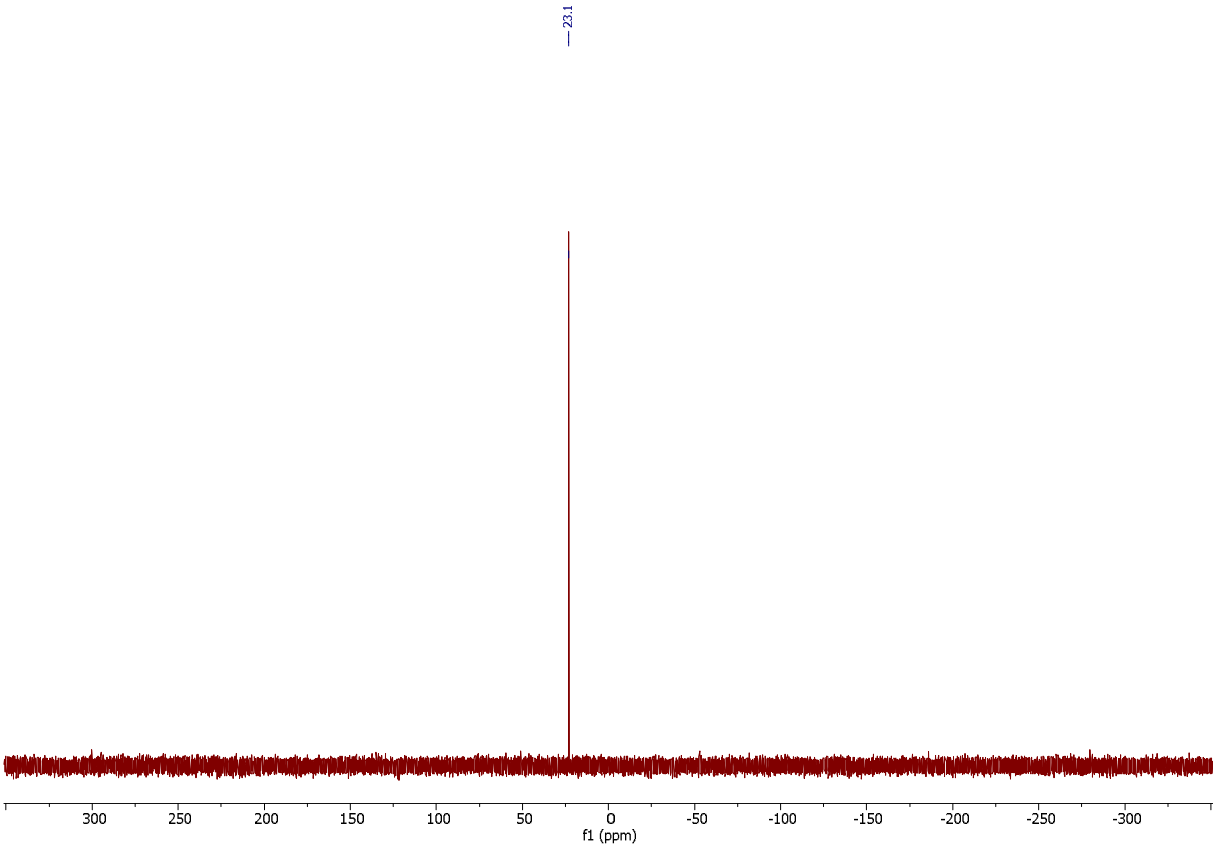

Figure S 4: ^{31}P NMR (CD_2Cl_2, 298 K) spectrum of 1-Cl.

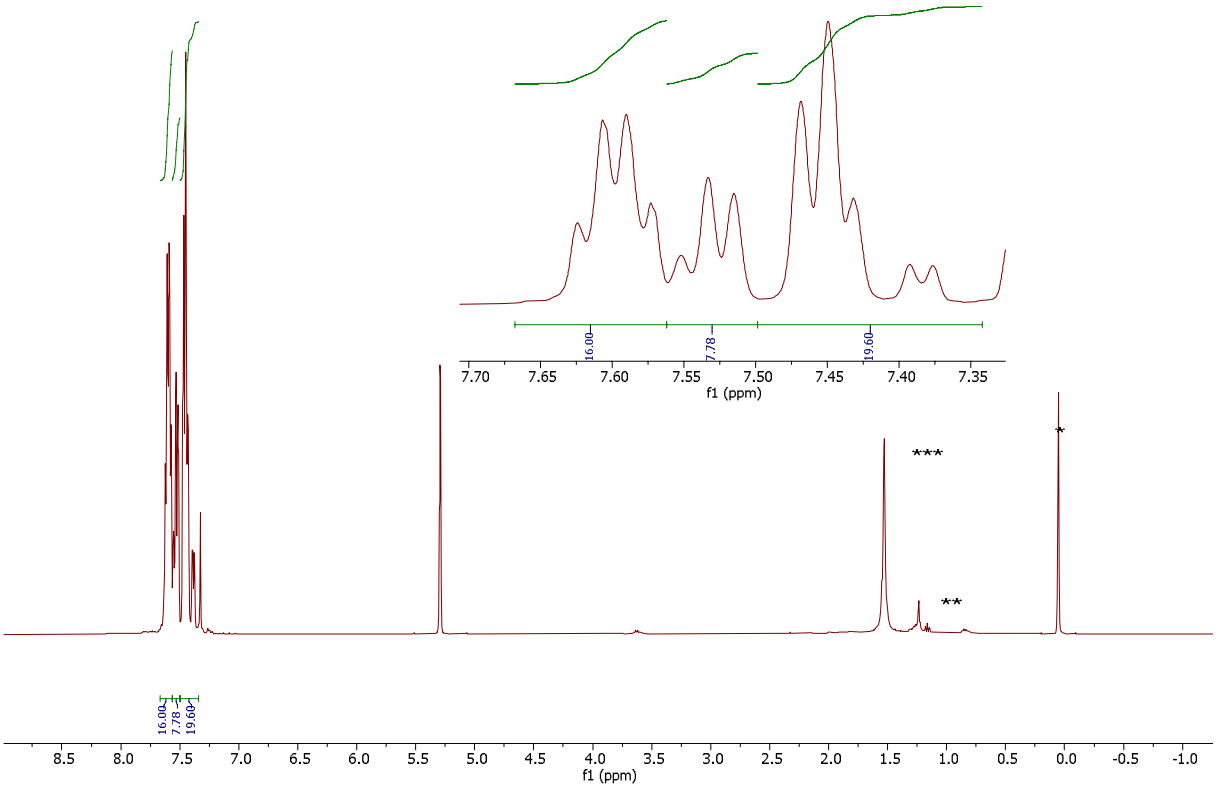

*Figure S 5: ^{1}H NMR ($CD2Cl_2$, 298 K) spectrum of 2. * silicon grease, ** grease, *** water*

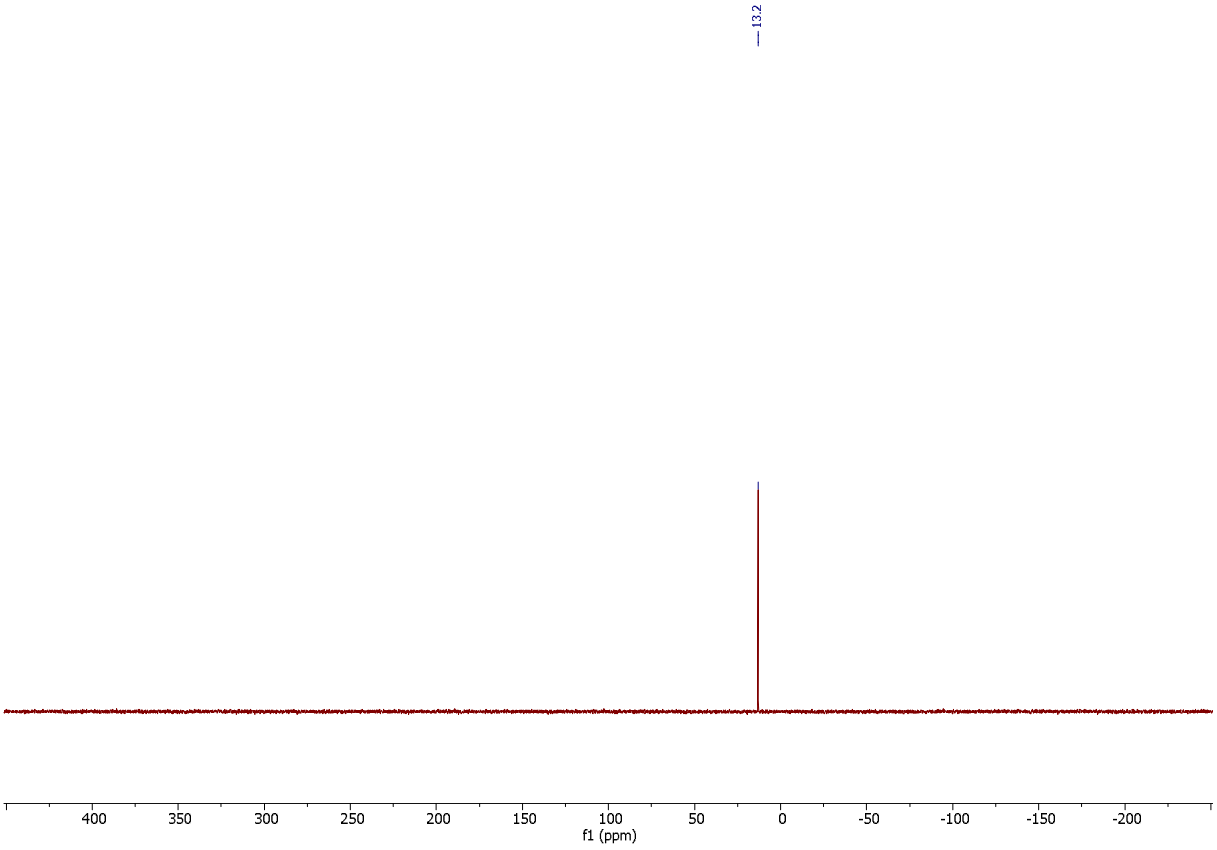

Figure S 6: ^{31}P NMR (CD_2Cl_2, 298 K) spectrum of 2.

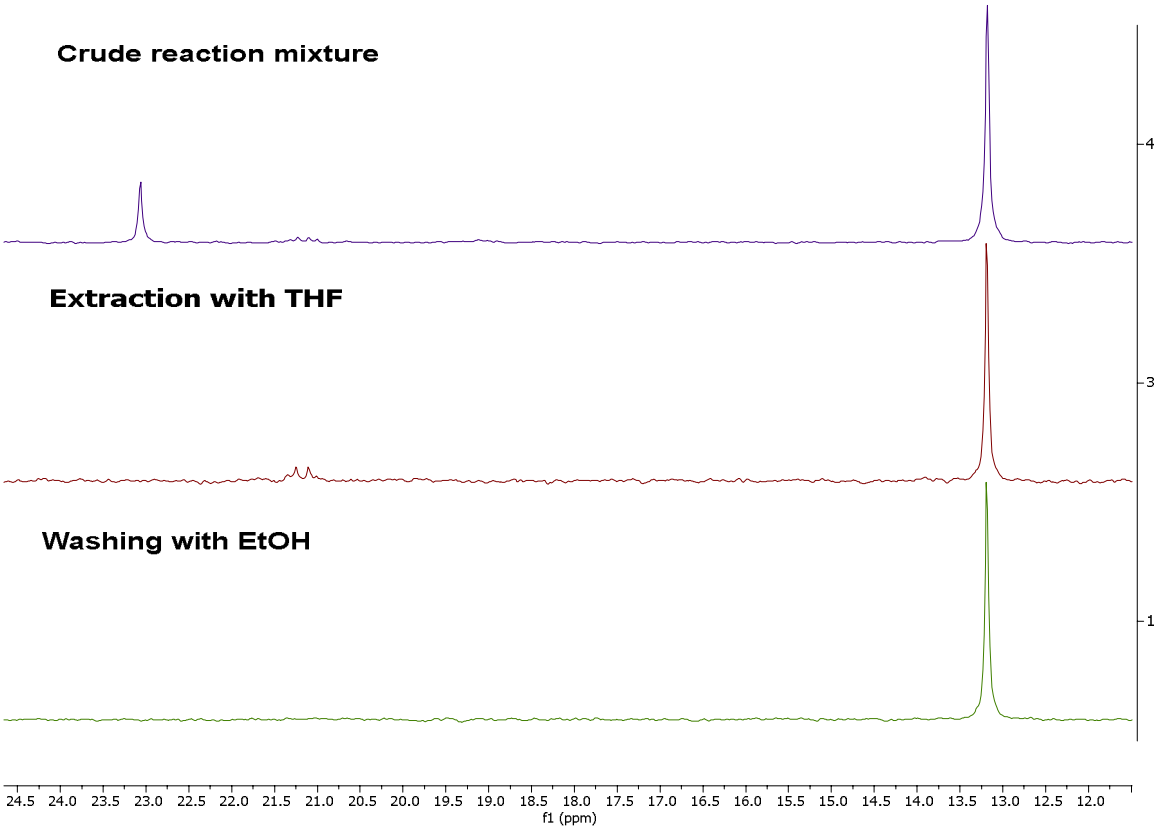

Figure S 7: Attempted preparation of 2 in chloroform and subsequent purification affording 1-Cl. ^{31}P-NMR of crude reaction, and after purification steps.

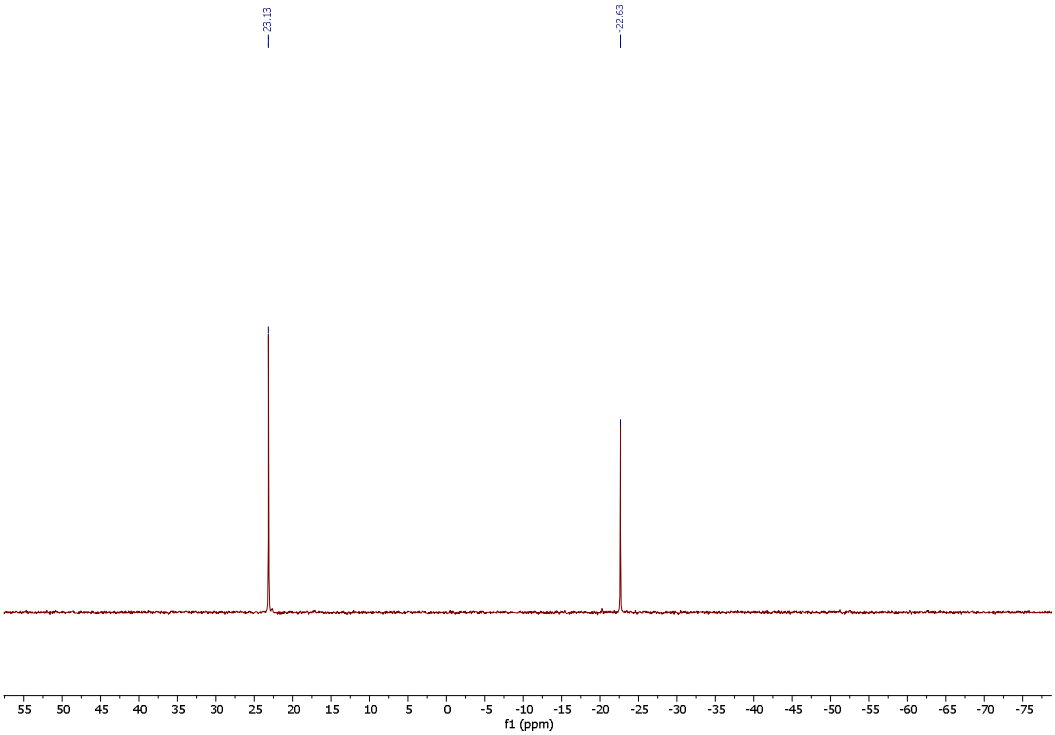

Figure S 8: Attempted synthesis of dinuclear complex 3. ^{31}P-NMR of crude reaction mixture before solvent evaporation showing a mixture of 1-Cl and 3.