# Axially Chiral Allenyl Gold Complexes

Alice Johnson, Antonio Laguna and M. Concepción Gimeno*

gimeno@unizar.es

**Contents**

1. Experimental S2

1.1. Starting Materials S2

1.2. Instrumentation S2

1.3. Synthesis of [AuBr{C($PPh_3$)C=$CH_2$}] (**1**) S2

1.4. Synthesis of [Au($C_6F_5$){C($PPh_3$)C=$CH_2$}] (**2**) S2

1.5. Synthesis of [Au($PPh_3$){C($PPh_3$)C=$CH_2$}]OTf (**3**) S3

1.6. Synthesis of [$Ph_3PCH_2C{\equiv}CH$][AuBr($C_6F_5$)$_3$] **(4a)** S3

1.7. Synthesis of [$Ph_3PCH{=}C{=}CH_2$][AuBr($C_6F_5$)$_3$] (**4b**) S4

1.8. Synthesis of [Au($C_6F_5$)$_3$ {CH=C=CH($PPh_3$)}] ((±)-**5**) S4

1.9. Crystallography S5

1.10. Structure of complex **3** (**Figure S1**)
S5

1.11. Protodesauration Experiment with Complex **3** S6

1.12. Variable Temperature NMR experiment for Complex **1** in thf S7

1.13. Stability Experiment Complex **3** S8

1.14. References S10

**Table S1.** $^{1}$H and $^{31}$P NMR signals for triphenylpropargylphosphonium bromide in various solvents S11

**Table S2.** Crystal data and structure refinement for **1** S12

**Table S3.** Bond lengths [A] and angles [deg] for complex **1** S13

**Table S4.** Crystal data and structure refinement for **2**. S16

**Table S5.** Bond lengths [A] and angles [deg] for complex **2**. S17

**Table S6.** Crystal data and structure refinement for **3** S19

**Table S7.** Bond lengths [A] and angles [deg] for complex **3** S20

**Table S8.** Crystal data and structure refinement for (±)-**5**. S25

**Table S9**. Bond lengths [A] and angles [deg] for complex **(±)-5**. S26

# 1. Experimental

## 1.1. Starting Materials

The starting materials [AuCl(tht)],[1] [Au($C_6F_5$)(tht)],[2] [Au($C_6F_5$)$_3$(tht)],[3] and [AuCl($PPh_3$)][4] were prepared according to published procedures. [$Ph_3PCH_2C{\equiv}CH$]Br was purchased from TCI and used as received. All other reagents were commercially available and were used without further purification. Solvents were dried with a SPS solvent purification system.

## 1.2. Instrumentation

Mass spectra were recorded on a Bruker Esquire 3000 PLUS, with the electrospray (ESI) technique and on a Bruker Microflex (MALDI-TOF). $^1$H, $^{13}$C{H} and $^{19}$F NMR, including 2D experiments, were recorded at room temperature on a Bruker Avance 400 spectrometer ($^1$H, 400 MHz, $^{13}$C, 100.6 MHz, $^{19}$F, 376.5 MHz) or on a Bruker Avance II 300 spectrometer ($^1$H, 300 MHz, $^{13}$C, 75.5 MHz, $^{19}$F, 282.3 MHz), with chemical shifts (δ, ppm) reported relative to the solvent peaks of the deuterated solvent. All *J* values are given in Hz. IR spectra were recorded in neat samples on a Perkin-Elmer Spectrum 100 FT-IR spectrometer.

## 1.3. Synthesis of [AuBr{C($PPh_3$)C=$CH_2$}] (1)

[$Ph_3PCH_2C{\equiv}CH$]Br (0.0763 g, 0.2 mmol) and [AuCl(tht)] (0.0321 g, 0.1 mmol) were stirred in $CH_2Cl_2$ (20 ml) for 4 h at room temperature with excess $Cs_2CO_3$. The mixture was filtered through celite and the resulting orange solution concentrated under reduced pressure to approximately 2 ml. The product was precipitated with ethanol, collected by vacuum filtration and dried to give **1** as an orange solid (0.0364 g, 63 %). IR (cm$^{-1}$) ν(C=$\underline{CH_2}$) 3068, ν(C=C=C) 1906. $^1$H NMR ($CDCl_3$, 400.16 MHz) δ 7.54 – 7.76 (m, 15 H, Ph), 4.09 (d, $^4J_{HP}$ = 16.0 Hz, 2 H, $CH_2$). $^{31}$P NMR ($CDCl_3$, 161.99 MHz) δ 17.30 (s, $PPh_3$). $^{13}$C APT ($CDCl_3$, 75.48 MHz) δ 216.54 (s, C=$\underline{C}$=C), 133.95 (d, $^3J_{CP}$ = 9.0 Hz, *m*-$Ph_3P$), 133.72, (d, $^4J_{CP}$ = 2.9 Hz, *p*-$Ph_3P$), 129.30 (d, $^2J_{CP}$ = 12.4 Hz, *o*-$Ph_3P$), 122.44 (d, $^1J_{CP}$ = 89.1 Hz, *ipso*-$Ph_3P$), 83.88 (d, $^1J_{CP}$ = 50.2 Hz, $\underline{C}$($PPh_3$)), 65.63 (d, $^3J_{CP}$ = 20.9 Hz, $CH_2$).

## 1.4. Synthesis of [Au($C_6F_5$){C($PPh_3$)C=$CH_2$}] (2)

[Au($C_6F_5$)(tht)] (0.0452 g, 0.1 mmol) and [$Ph_3PCH_2C{\equiv}CH$]Br (0.0381 g, 0.1 mmol) were stirred in $CH_2Cl_2$ (20 ml) for 3 h at room temperature with excess $Cs_2CO_3$. The

mixture was filtered through celite and the resulting pale yellow solution concentrated under reduced pressure to approximately 2 ml. The product was precipitated with ethanol, collected by vacuum filtration and dried to give a pale yellow solid (0.0566 g, 85 %). IR ($cm^{-1}$) ν(C=$\underline{CH_2}$) 3055, ν(C=C=C) 1901, ν($C_6F_5$) 1500, 953, 794. $^1$H NMR ($CDCl_3$, 400.16 MHz) δ 7.39 – 7.83 (m, 15 H, Ph), 4.12 (d, $^4J_{HP}$ = 16.0 Hz, 2 H, $CH_2$). $^{31}$P NMR ($CDCl_3$, 161.99 MHz) δ 19.14 (s, $PPh_3$). $^{19}$F NMR ($CDCl_3$, 376.48 MHz) δ -115.77 – -115.92 (m, 2 F, *o*-$C_6F_5$), -161.14 (t, $^3J_{FF}$ = 20.3 Hz, 1 F, *p*-$C_6F_5$), -163.28 – -163.43 (m, 2 F, *m*-$C_6F_5$). $^{13}$C APT ($CDCl_3$, 75.48 MHz) 215.98 (s, C=$\underline{C}$=C), 134.22 (d, $^3J_{CP}$ = 9.0 Hz, *m*-$Ph_3P$), 133.71 (d, $^4J_{CP}$ = 2.9 Hz, *p*-$Ph_3P$), 129.40 (d, $^2J_{CP}$ = 12.3 Hz, *o*-$Ph_3P$), 123.32 (d, $^1J_{CP}$ = 88.5 Hz, *ipso*-$Ph_3P$), 64.00 (d, $^3J_{CP}$ = 22.2 Hz, $CH_2$).

### 1.5. Synthesis of [Au(PPh$_3$){C(PPh$_3$)C=CH$_2$}](OTf) (3)

Method 1: [$Ph_3PCH_2C$≡CH]Br (0.0450 g, 0.1 mmol) and [Au(acac)($PPh_3$)] (0.0559 g, 0.1 mmol) were stirred in $CH_2Cl_2$ (20 ml) for 1 h at room temperature. The mixture was filtered through celite and the resulting yellow solution concentrated under reduced pressure to 2 ml. The product was precipitated with *n*-hexane, collected by vacuum filtration and dried to give **3** as an orange solid (0.0526 g, 58 %).

Method 2: **2** (0.0664 g, 0.1 mmol) and [Au($PPh_3$)$_2$]OTf (0.0870 g, 0.1 mmol) were stirred in $CH_2Cl_2$ (20 ml) for 30 min at room temperature. The mixture was filtered through celite and the resulting colourless solution concentrated under reduced pressure to approximately 2 ml. The product was precipitated with diethyl ether, collected by vacuum filtration and dried to give **3** as a white solid (0.0452 g, 50 %). IR ($cm^{-1}$) ν(C=$\underline{CH_2}$) 3054, ν(C=C=C) 1911, (OTf) 1266 ($SO_3$), 1225 ($CF_3$), 1159 ($CF_3$), 1030 ($SO_3$). $^1$H NMR ($CDCl_3$, 400.16 MHz) δ 4.50 (d, $^4J_{HP}$ = 15.6 Hz, 2 H, $CH_2$), 7.44 – 7.80 (m, 30 H, Ph). $^{31}$P NMR ($CDCl_3$, 161.99 MHz) δ 19.85 (s, $\underline{P}Ph_3$), 40.24 (s, Au$\underline{P}Ph_3$). $^{19}$F NMR ($CDCl_3$, 376.48 MHz): δ -77.98 (s, OTf). $^{13}$C APT ($CDCl_3$, 75.48 MHz) δ 134.64 (d, $^4J_{CP}$ = 2.9 Hz, *p*-$PPh_3$), 134.04 (d, $^2J_{CP}$ = 13.6 Hz, *o*-$PPh_3$), 133.91 (d, $^3J_{CP}$ = 9.1 Hz, *m*-$PPh_3$), 132.36 (d, $^4J_{CP}$ = 2.5 Hz, *p*-$PPh_3$), 130.00 (d, $^2J_{CP}$ = 12.4 Hz, *o*-$Ph_3P$), 129.67 (d, $^3J_{CP}$ = 11.5 Hz, *m*-$Ph_3P$), 128.61 (d, $^1J_{CP}$ = 57.1 Hz, *ipso*-$Ph_3P$), 122.04 (d, $^1J_{CP}$ = 90.6 Hz, *ipso*-$Ph_3P$), 66.52 (d, $^3J_{CP}$ = 21.1 Hz, $CH_2$).

### 1.6. Synthesis of [Ph$_3$PCH$_2$C≡CH][AuBr(C$_6$F$_5$)$_3$] (4a)

[$Ph_3PCH_2C$≡CH]Br (0.1372 g, 0.36 mmol) and [Au($C_6F_5$)$_3$(tht)] (0.2839 g, 0.36 mmol) were stirred in $CH_2Cl_2$ (20 ml) overnight at room temperature. The colourless solution

was concentrated under reduced pressure to 2 ml. The product was precipitated with *n*-hexane, collected by vacuum filtration and dried to give **4a** as a white solid (0.3782 g, 97 %). IR ($cm^{-1}$) ν(C≡C-H) 3305, ν(C≡C) 2214, ν($C_6F_5$) 1505, 963, 793. $^1$H NMR ($CDCl_3$, 400.16 MHz) δ 7.67 – 7.92 (m, 15 H, Ph), 4.18 (dd, $^2J_{HP}$ = 14.8 Hz, $^4J_{HH}$ = 2.4 Hz, 2 H, $CH_2$), 2.37 (dt, $^4J_{HP}$ = 6.8, $^4J_{HH}$ = 2.4, 1 H, CH). $^{31}$P NMR ($CDCl_3$, 161.99 MHz) δ 21.26 (s, $PPh_3$). $^{19}$F NMR ($CDCl_3$, 376.48 MHz) δ -120.93 – -121.04 (m, 4 F, *o*-$C_6F_5$), -121.78 – -121.88 (m, 2 F, *o*-$C_6F_5$), -158.82 (t, $^3J_{FF}$ = 18.8, 1 F, *p*-$C_6F_5$), -159.91 (t, $^3J_{FF}$ = 18.8, 2 F, *p*-$C_6F_5$), -162.31 – -162.44 (m, 2 F, *m*-$C_6F_5$), -162.69 – -162.84 (m, 4 F, *m*-$C_6F_5$). $^{13}$C APT (101 MHz, $CDCl_3$) δ 136.33 (d, $^4J_{CP}$ = 2.9 Hz, *p*-$PPh_3$), 133.62 (d, $^3J_{CP}$ = 10.1 Hz, *m*-$PPh_3$), 130.93 (d, $^2J_{CP}$ = 13.0 Hz, *o*-$PPh_3$), 116.52 (d, $^1J_{CP}$ = 88.0 Hz, *ipso*-Ph), 77.77 (d, $^3J_{CP}$ = 9.6 Hz, CH), 70.21 (d, $^2J_{CP}$ = 12.1 Hz, C≡CH), 17.84 (d, $^1J_{CP}$ = 58.4 Hz, $CH_2$).

### 1.7. Synthesis of [$Ph_3PCH{=}C{=}CH_2$][$AuBr(C_6F_5)_3$] (4b)

**4a** (0.1079 g, 0.1 mmol) was stirred in $CH_2Cl_2$ (20 ml) for 2 h at room temperature with excess $Cs_2CO_3$. The mixture was filtered through celite and the resulting yellow solution concentrated under reduced pressure to 2 ml. The product was precipitated with *n*-hexane, collected by vacuum filtration and dried to give **4b** as a pale orange solid (0.0486 g, 45 %). IR ($cm^{-1}$) ν(C=$CH_2$) 3063, ν(C=C=C) 1914, ν($C_6F_5$) 1504, 963, 793. $^1$H NMR ($CDCl_3$, 400.16 MHz) δ 7.52 – 7.89 (m, 15 H, Ph), 6.45 (dt, $^2J_{HP}$ = 8.4 Hz, $^4J_{HH}$ = 6.8 Hz, 1 H, CH), 5.36 (dd, $^4J_{HP}$ = 12.8 Hz, $^4J_{HH}$ = 6.8 Hz, 2 H, $CH_2$). $^{31}$P NMR ($CDCl_3$, 161.99 MHz) δ 18.29 (s, $PPh_3$). $^{19}$F NMR ($CDCl_3$, 376.48 MHz) δ -120.80 – -120.89 (m, 4 F, *o*-$C_6F_5$), -121.71 – -121.84 (m, 2 F, *o*-$C_6F_5$), -158.98 (t, $^3J_{FF}$ = 20.1 Hz, 1 F, *p*-$C_6F_5$), -160.14 (t, $^3J_{FF}$ = 19.7 Hz, 2 F, *p*-$C_6F_5$), -162.42 – -162.56 (m, 2 F, *m*-$C_6F_5$), -162.87 – -163.03 (m, 4 F, *m*-$C_6F_5$).

### 1.8. Synthesis of [$Au(C_6F_5)_3${CH=C=CH($PPh_3$)}] ((±)-5)

Method 1: **4a** (0.0810 g, 0.075 mmol) was stirred in $Et_2O$ (20 ml) for 2 h at room temperature with excess NaH. The mixture was filtered through celite and the resulting yellow solution concentrated under reduced pressure to 2 ml. The product was precipitated with *n*-hexane, collected by vacuum filtration and dried to give (±)-**5** as an orange solid (0.0490 g, 65 %).

Method 2: [$Ph_3PCH{=}C{=}CH_2$]OTf (0.0901 g, 0.2 mmol) and [$Au(C_6F_5)_3$(tht)] (0.1573 g, 0.2 mmol) were stirred in $CH_2Cl_2$ (20 ml) for 30 min at room temperature with excess

$Cs_2CO_3$. The mixture was filtered through celite and the resulting orange/brown solution concentrated under reduced pressure to 2 ml. The product was precipitated with *n*-hexane, collected by vacuum filtration and dried to give **5** as an orange solid (0.1013 g, 51 %). IR ($cm^{-1}$) ν(C=C=C) 1907, ν($C_6F_5$) 1504, 963, 793. $^1$H NMR ($CDCl_3$, 400.16 MHz) δ 7.42 – 7.89 (m, 15 H, Ph), 5.84 (dd, $^4J_{HP}$ = 12.8 Hz, $^4J_{HH}$ = 6.0 Hz, 1 H, Au-C<u>H</u>), 4.88 (dd, $^2J_{HP}$ = 14.0 Hz, $^4J_{HH}$ = 6.0 Hz, 1 H, C<u>H</u>($PPh_3$)). $^{31}$P NMR ($CDCl_3$, 161.99 MHz) δ 17.86 (s, $PPh_3$). $^{19}$F NMR ($CDCl_3$, 376.48 MHz) δ -121.41 – -121.75 (m, *o*-$C_6F_5$), -154.39 (t, $^3J_{FF}$ = 20.0 Hz, *p*-$C_6F_5$), -155.74 (t, $^3J_{FF}$ = 20.3 Hz, *p*-$C_6F_5$), -159.14 – -159.35 (m, *m*-$C_6F_5$), -160.36 – -160.47 (m, *m*-$C_6F_5$). 13C NMR (75 MHz, CDCl3) δ 205.63 (s, C=<u>C</u>=C), 147.41 – 146.96 (m, $C_6F_5$), 144.39 – 143.88 (m, $C_6F_5$), 140.24 – 139.86 (m, $C_6F_5$), 139.21 – 138.68 (m, $C_6F_5$), 136.98 – 136.61 (m, $C_6F_5$), 135.64 – 135.34 (m, $C_6F_5$), 134.92 (d, $^4J_{CP}$ = 2.9 Hz, *p*-$PPh_3$), 133.44 (d, $^3J_{CP}$ = 10.2 Hz, *m*-$PPh_3$), 130.15 (d, $^2J_{CP}$ = 12.9 Hz, *o*-$PPh_3$) 119.97 (d, $^1J_{CP}$ = 91.3 Hz, *ipso*-$PPh_3$), 86.41 (d, $^3J_{CP}$ = 15.1 Hz, Au-<u>C</u>H), 60.45 (d, $^1J_{CP}$ = 104.3 Hz, <u>C</u>H($PPh_3$)).

### 1.9. Crystallography

Crystals were obtained by slow diffusion of hexane or diethyl ether over a solution of the corresponding complex in dichloromethane. Crystals were mounted in inert oil on glass fibres and transferred to the cold gas stream of an Xcalibur Oxford Diffraction diffractometer equipped with a low-temperature attachment. Data were collected using monochromated Mo Kα radiation (λ = 0.71073 Å). Scan type ω. Absorption corrections based on multiple scans were applied with the program SADABS[5] or using spherical harmonics implemented in SCALE3 ABSPACK[6] scaling algorithm. The structures were solved by direct methods and refined on $F^2$ using the program SHELXL-97.[7] All non-hydrogen atoms were refined anisotropically. In most of the cases, hydrogen atoms were included in calculated positions and refined using a riding model; some of the hydrogen atoms have been located in the diffraction map. Refinements were carried out by full-matrix least-squares on $F^2$ for all data.

### 1.10. Structure of complex 3 (Figure S1)

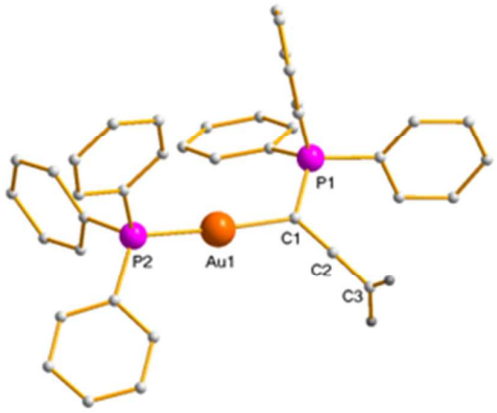
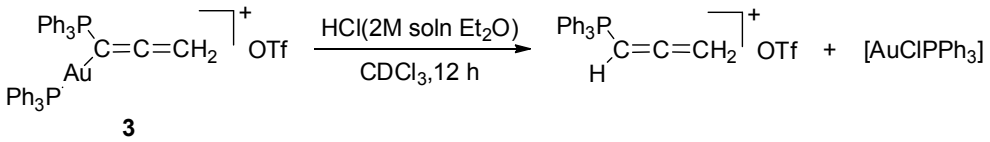
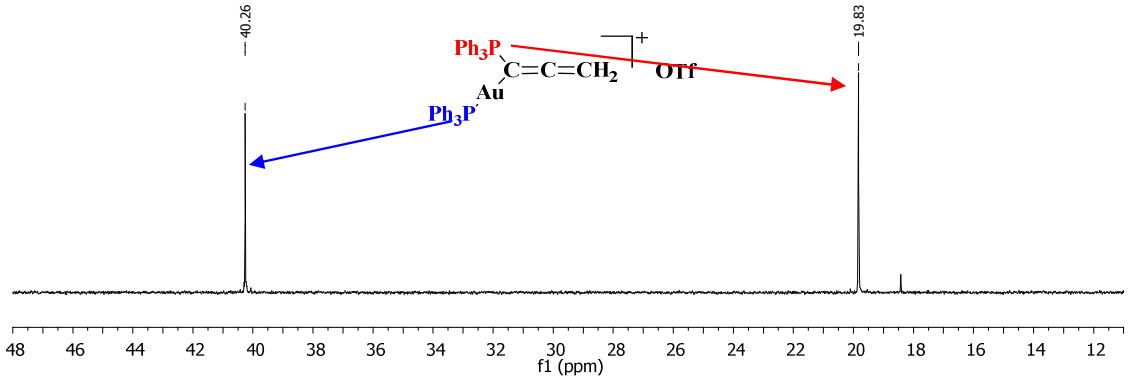



**Figure S1.** Structure of complex **3**

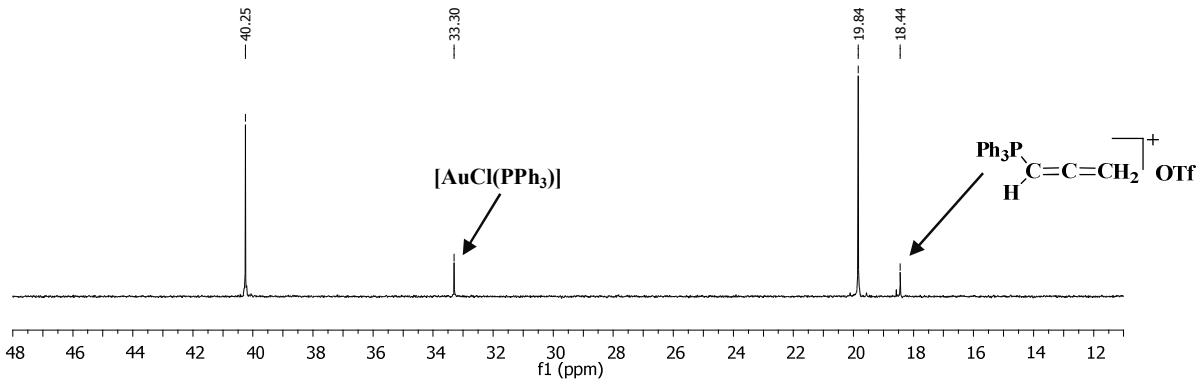
## 1.11. Protodesauration Experiment with Complex 3



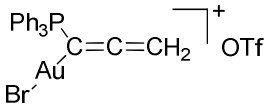

$^{31}$P NMR spectrum complex **3**:



$^{31}$P NMR spectrum of complex **3** following 5 h with HCl:

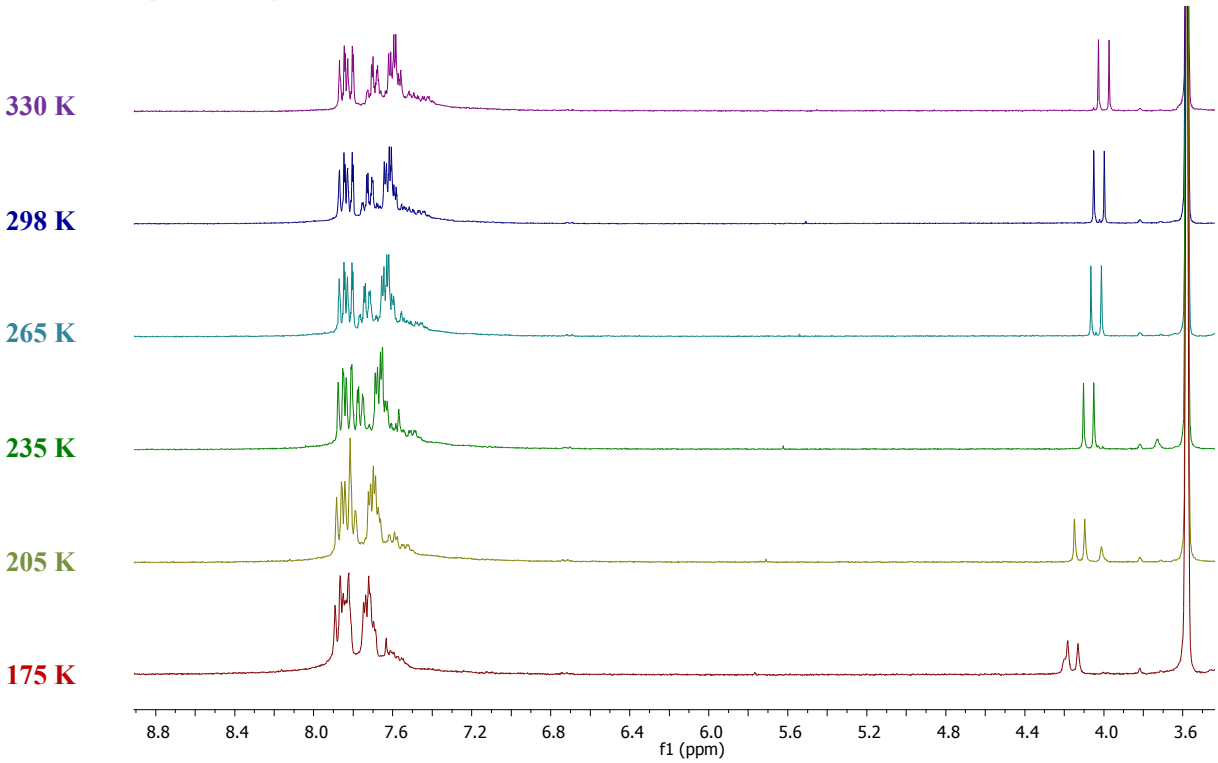



**1.12. Variable Temperature NMR experiment for Complex 1 in thf**

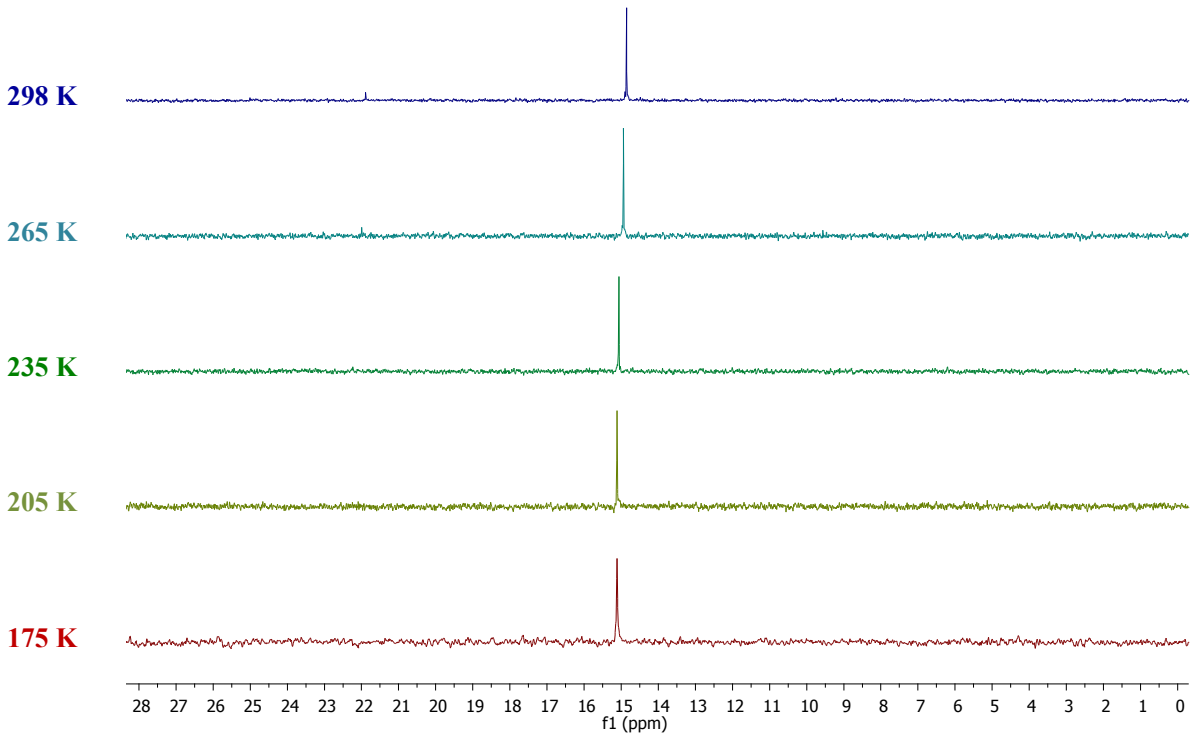



**1**

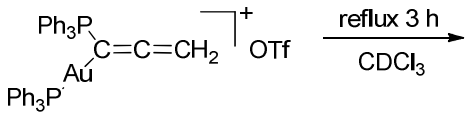
$^{1}$H NMR spectra complex **1** in thf:



$^{31}$P NMR spectra complex **1** in thf:

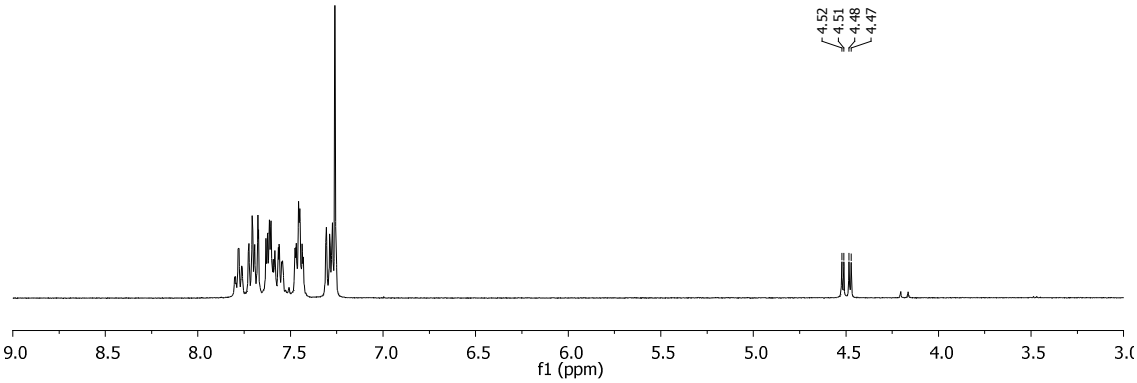



### 1.13. Stability Experiment Complex 3

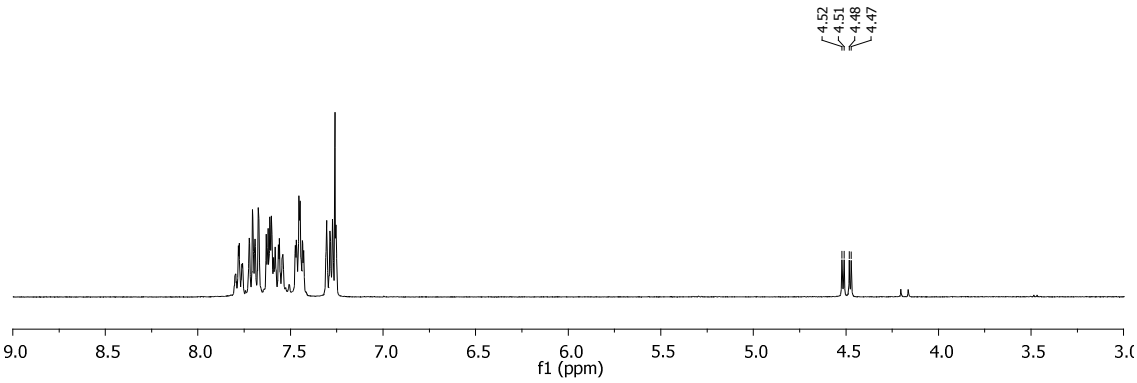



**3**

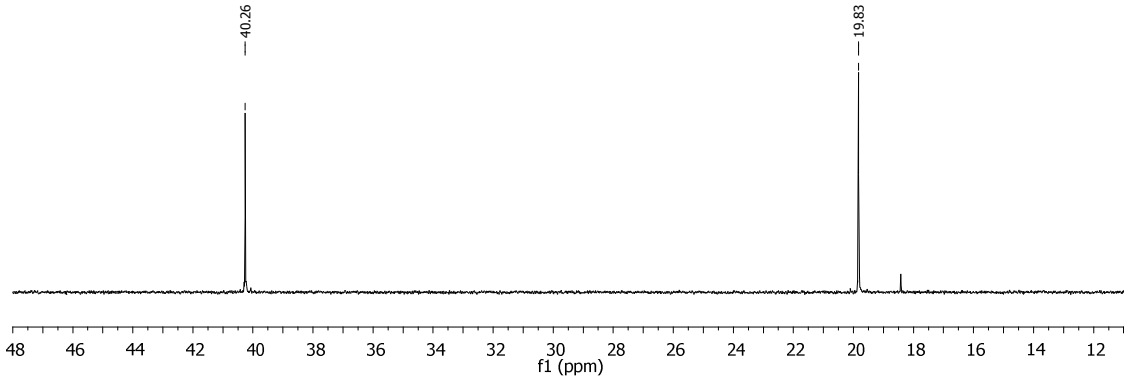
$^{1}$H NMR spectrum complex **3** $CDCl_3$:



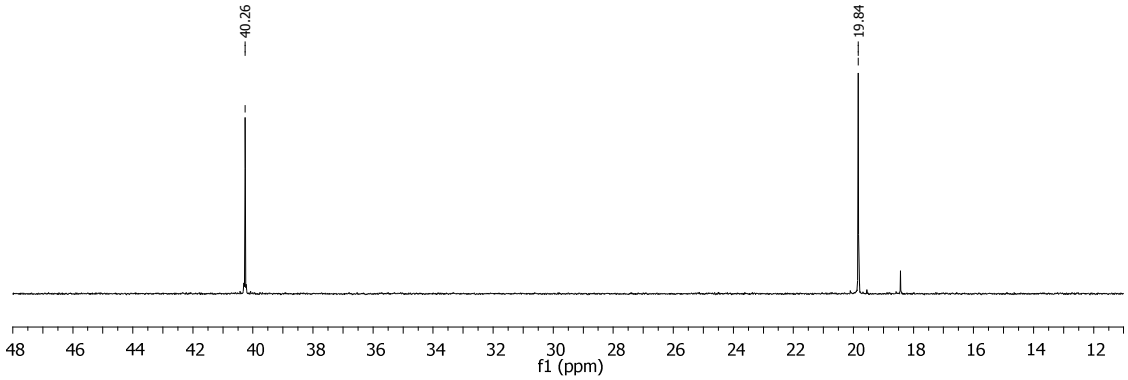
$^{1}$H NMR spectrum complex **3** $CDCl_3$ following 3 h under reflux:




$^{31}$P NMR spectrum complex **3** $CDCl_3$:




$^{31}$P NMR spectrum complex **3** $CDCl_3$ following 3 h under reflux:



## 1.14. References


1. Uson, R.; Laguna, A. *Inorg. Synth.* **1982**, *21*, 71.
2. Uson, R.; Laguna, A.; Laguna, M. *Inorg. Synth*. **1989**, *26*, 85.
3. Uson, R.; Laguna, A.; Laguna, M.; Fernández, E.; Jones, P. G.; Sheldrick, G. M. *J. Chem. Soc. Chem. Commun.* **1982**, 1971.
4. Al-Saady, A. K.; McAuliffe, C. A.; Parish, R. V.; Sandbank, J. A. *Inorg. Synth*., **1985**, *23*, 191.
5. Sheldrick, G. M. SADABS, *Program for absorption correction*, University of Göttingen, Göttingen, Germany, 1996.
6. CrysAlisPro, Agilent Technologies, Version 1.171.35.11. Multi-scans absorption correction with SCALE3 ABSPACK scaling algorithm.
7. Sheldrick, G. M. SHELXL-97, *Program for Crystal Structure Refinement*, University of Göttingen, Göttingen, Germany, 1997.

**Table S1.** $^{1}$H and $^{31}$P NMR signals for triphenylpropargylphosphonium bromide in various solvents

| Solvent | $^{1}$H NMR δ (ppm)[a] | $^{31}$P NMR δ (ppm) |
|---|---|---|
| DMSO | 3.46 dt (1H, $^{4}J_{HP}$ = 6.8 Hz, $^{4}J_{HH}$ = 2.8 Hz)<br>5.11 dd (2H, $^{2}J_{HP}$ = 16.4 Hz, $^{4}J_{HH}$ = 2.8 Hz) | 22.10 |
| Chloroform | 5.25 dd (2H, $^{4}J_{HP}$ = 13.2 Hz, $^{4}J_{HH}$ = 6.4 Hz)<br>8.27 dt (1H, $^{2}J_{HP}$ = 7.2 Hz, $^{4}J_{HH}$ = 6.4 Hz) | 19.19 |
| Acetonitrile | 5.35 dd (2H, $^{4}J_{HP}$ = 13.2 Hz, $^{4}J_{HH}$ = 6.8 Hz)<br>6.67 dt (1H, $^{2}J_{HP}$ = 7.2 Hz, $^{4}J_{HH}$ = 6.8 Hz) | 18.57 |
| Acetone | 5.56 dd (2H, $^{4}J_{HP}$ = 13.2 Hz, $^{4}J_{HH}$ = 6.8 Hz)<br>7.16 dt (1H, $^{4}J_{HP}$ = 7.2 Hz, $^{4}J_{HH}$ = 6.8 Hz) | 19.45 |
| Dichloromethane | 5.33 dd (2H, $^{4}J_{HP}$ = 12.8 Hz, $^{4}J_{HH}$ = 6.8 Hz)<br>7.48 dt (1H, $^{2}J_{HP}$ = 7.2 Hz, $^{4}J_{HH}$ = 6.8 Hz) | 18.77 |

[a]Signals for aromatic protons not shown.

**Table S2.** Crystal Data for complex **1**

| | |
|---|---|
| Empirical formula | $C_{21}H_{17}AuBrP$ |
| Formula weight | 577.19 |
| Temperature | 103(2) K |
| Wavelength | 0.71073 A |
| Crystal system, space group | Triclinic, P-1 |
| Unit cell dimensions | a = 7.9385(2) A alpha = 97.371(2) deg.<br>b = 10.9763(3) A beta = 99.927(2) deg.<br>c = 11.4409(3) A gamma = 100.842(2) deg. |
| Volume | 951.05(4) A^3 |
| Z, Calculated density | 2, 2.016 Mg/m^3 |
| Absorption coefficient | 9.918 mm^-1 |
| F(000) | 544 |
| Crystal size | 0.42 x 0.40 x 0.20 mm |
| Theta range for data collection | 4.41 to 25.50 deg. |
| Limiting indices | -9<=h<=9, -13<=k<=13, -13<=l<=13 |
| Reflections collected / unique | 17664 / 3532 [R(int) = 0.0429] |
| Completeness to theta = 25.50 | 99.5 % |
| Absorption correction | Semi-empirical from equivalents |
| Max. and min. transmission | 0.2417 and 0.1031 |
| Refinement method | Full-matrix least-squares on F^2 |
| Data / restraints / parameters | 3532 / 0 / 225 |
| Goodness-of-fit on F^2 | 1.076 |
| Final R indices [I>2sigma(I)] | R1 = 0.0199, wR2 = 0.0518 |
| R indices (all data) | R1 = 0.0204, wR2 = 0.0521 |
| Largest diff. peak and hole | 1.905 and -1.392 e.A^-3 |

**Table S3.** Bond lengths [A] and angles [deg] for complex **1**.

| | | | |
|---|---|---|---|
| Au(1)-C(1) | 2.032(4) | C(21)-C(26) | 1.394(5) |
| Au(1)-Br(1) | 2.3980(4) | C(22)-C(23) | 1.385(5) |
| C(1)-C(2) | 1.296(5) | C(22)-H(22) | 0.9500 |
| C(1)-P(1) | 1.769(3) | C(23)-C(24) | 1.389(5) |
| C(2)-C(3) | 1.304(5) | C(23)-H(23) | 0.9500 |
| C(3)-H(2) | 0.86(5) | C(24)-C(25) | 1.384(5) |
| C(3)-H(1) | 0.98(5) | C(24)-H(24) | 0.9500 |
| P(1)-C(21) | 1.792(3) | C(25)-C(26) | 1.374(5) |
| P(1)-C(11) | 1.795(3) | C(25)-H(25) | 0.9500 |
| P(1)-C(31) | 1.803(3) | C(26)-H(26) | 0.9500 |
| C(11)-C(16) | 1.395(5) | C(31)-C(36) | 1.379(5) |
| C(11)-C(12) | 1.399(5) | C(31)-C(32) | 1.396(5) |
| C(12)-C(13) | 1.380(5) | C(32)-C(33) | 1.384(5) |
| C(12)-H(12) | 0.9500 | C(32)-H(32) | 0.9500 |
| C(13)-C(14) | 1.380(6) | C(33)-C(34) | 1.381(6) |
| C(13)-H(13) | 0.9500 | C(33)-H(33) | 0.9500 |
| C(14)-C(15) | 1.386(6) | C(34)-C(35) | 1.389(6) |
| C(14)-H(14) | 0.9500 | C(34)-H(34) | 0.9500 |
| C(15)-C(16) | 1.385(5) | C(35)-C(36) | 1.373(5) |
| C(15)-H(15) | 0.9500 | C(35)-H(35) | 0.9500 |
| C(16)-H(16) | 0.9500 | C(36)-H(36) | 0.9500 |
| C(21)-C(22) | 1.392(5) | | |

| | |
|---|---|
| C(1)-Au(1)-Br(1) | 179.66(10) |
| C(2)-C(1)-P(1) | 119.5(3) |
| C(2)-C(1)-Au(1) | 125.0(3) |
| P(1)-C(1)-Au(1) | 115.46(18) |
| C(1)-C(2)-C(3) | 178.6(4) |
| C(2)-C(3)-H(2) | 117(3) |
| C(2)-C(3)-H(1) | 124(3) |
| H(2)-C(3)-H(1) | 119(4) |
| C(1)-P(1)-C(21) | 108.88(16) |
| C(1)-P(1)-C(11) | 111.19(15) |
| C(21)-P(1)-C(11) | 108.26(16) |
| C(1)-P(1)-C(31) | 112.81(16) |
| C(21)-P(1)-C(31) | 109.27(15) |
| C(11)-P(1)-C(31) | 106.30(17) |
| C(16)-C(11)-C(12) | 120.2(3) |
| C(16)-C(11)-P(1) | 120.9(3) |
| C(12)-C(11)-P(1) | 118.7(3) |
| C(13)-C(12)-C(11) | 119.8(3) |
| C(13)-C(12)-H(12) | 120.1 |
| C(11)-C(12)-H(12) | 120.1 |
| C(12)-C(13)-C(14) | 119.8(3) |
| C(12)-C(13)-H(13) | 120.1 |
| C(14)-C(13)-H(13) | 120.1 |
| C(13)-C(14)-C(15) | 120.9(3) |
| C(13)-C(14)-H(14) | 119.6 |
| C(15)-C(14)-H(14) | 119.6 |
| C(16)-C(15)-C(14) | 120.1(4) |
| C(16)-C(15)-H(15) | 120.0 |
| C(14)-C(15)-H(15) | 120.0 |
| C(15)-C(16)-C(11) | 119.3(3) |
| C(15)-C(16)-H(16) | 120.4 |
| C(11)-C(16)-H(16) | 120.4 |
| C(22)-C(21)-C(26) | 119.5(3) |
| C(22)-C(21)-P(1) | 119.4(3) |
| C(26)-C(21)-P(1) | 121.1(3) |
| C(23)-C(22)-C(21) | 120.2(3) |
| C(23)-C(22)-H(22) | 119.9 |
| C(21)-C(22)-H(22) | 119.9 |
| C(22)-C(23)-C(24) | 119.7(4) |
| C(22)-C(23)-H(23) | 120.2 |
| C(24)-C(23)-H(23) | 120.2 |
| C(25)-C(24)-C(23) | 120.2(3) |
| C(25)-C(24)-H(24) | 119.9 |
| C(23)-C(24)-H(24) | 119.9 |
| C(26)-C(25)-C(24) | 120.3(3) |
| C(26)-C(25)-H(25) | 119.8 |
| C(24)-C(25)-H(25) | 119.8 |
| C(25)-C(26)-C(21) | 120.1(3) |
| C(25)-C(26)-H(26) | 119.9 |
| C(21)-C(26)-H(26) | 119.9 |
| C(36)-C(31)-C(32) | 120.0(3) |
| C(36)-C(31)-P(1) | 118.9(3) |
| C(32)-C(31)-P(1) | 121.2(3) |
| C(33)-C(32)-C(31) | 119.4(4) |
| C(33)-C(32)-H(32) | 120.3 |
| C(31)-C(32)-H(32) | 120.3 |

| | | | |
|---|---|---|---|
| C(34)-C(33)-C(32) | 120.3(3) | C(36)-C(35)-C(34) | 120.1(4) |
| C(34)-C(33)-H(33) | 119.8 | C(36)-C(35)-H(35) | 120.0 |
| C(32)-C(33)-H(33) | 119.8 | C(34)-C(35)-H(35) | 120.0 |
| C(33)-C(34)-C(35) | 119.8(3) | C(35)-C(36)-C(31) | 120.4(4) |
| C(33)-C(34)-H(34) | 120.1 | C(35)-C(36)-H(36) | 119.8 |
| C(35)-C(34)-H(34) | 120.1 | C(31)-C(36)-H(36) | 119.8 |

**Table S4.** Crystal data and structure refinement for **2**.

| | |
|---|---|
| Identification code | c274 |
| Empirical formula | C27 H17 Au F5 P |
| Formula weight | 664.34 |
| Temperature | 100(2) K |
| Wavelength | 0.71073 A |
| Crystal system, space group | Monoclinic, P2(1)/n |
| Unit cell dimensions | a = 10.54400(10) A alpha = 90 deg. |
| | b = 14.6999(2) A beta = 93.2030(10) deg. |
| | c = 14.8620(2) A gamma = 90 deg. |
| Volume | 2299.95(5) A^3 |
| Z, Calculated density | 4, 1.919 Mg/m^3 |
| Absorption coefficient | 6.520 mm^-1 |
| F(000) | 1272 |
| Crystal size | 0.42 x 0.40 x 0.30 mm |
| Theta range for data collection | 4.27 to 25.49 deg. |
| Limiting indices | -12<=h<=12, -17<=k<=17, -17<=l<=18 |
| Reflections collected / unique | 22456 / 4257 [R(int) = 0.0240] |
| Completeness to theta = 25.49 | 99.5 % |
| Absorption correction | Semi-empirical from equivalents |
| Max. and min. transmission | 0.2451 and 0.1704 |
| Refinement method | Full-matrix least-squares on F^2 |
| Data / restraints / parameters | 4257 / 0 / 315 |
| Goodness-of-fit on F^2 | 1.111 |
| Final R indices [I>2sigma(I)] | R1 = 0.0153, wR2 = 0.0352 |
| R indices (all data) | R1 = 0.0166, wR2 = 0.0357 |
| Largest diff. peak and hole | 0.511 and -0.371 e.A^-3 |

**Table S5.** Bond lengths [A] and angles [deg] for complex **2**.

| | | | |
|---|---|---|---|
| Au(1)-C(11) | 2.036(2) | C(21)-C(26) | 1.392(4) |
| Au(1)-C(1) | 2.055(2) | C(21)-C(22) | 1.392(4) |
| C(1)-C(2) | 1.304(4) | C(22)-C(23) | 1.386(4) |
| C(1)-P(1) | 1.770(2) | C(23)-C(24) | 1.382(4) |
| C(2)-C(3) | 1.300(4) | C(24)-C(25) | 1.377(4) |
| C(11)-C(16) | 1.378(4) | C(25)-C(26) | 1.389(4) |
| C(11)-C(12) | 1.384(3) | C(31)-C(32) | 1.390(4) |
| C(12)-F(1) | 1.354(3) | C(31)-C(36) | 1.392(3) |
| C(12)-C(13) | 1.377(4) | C(32)-C(33) | 1.376(4) |
| C(13)-F(2) | 1.351(3) | C(33)-C(34) | 1.389(4) |
| C(13)-C(14) | 1.380(4) | C(34)-C(35) | 1.372(4) |
| C(14)-F(3) | 1.335(3) | C(35)-C(36) | 1.386(4) |
| C(14)-C(15) | 1.376(4) | C(41)-C(42) | 1.388(4) |
| C(15)-F(4) | 1.345(3) | C(41)-C(46) | 1.391(3) |
| C(15)-C(16) | 1.369(4) | C(42)-C(43) | 1.381(4) |
| C(16)-F(5) | 1.353(3) | C(43)-C(44) | 1.388(4) |
| P(1)-C(41) | 1.797(2) | C(44)-C(45) | 1.374(4) |
| P(1)-C(31) | 1.799(2) | C(45)-C(46) | 1.391(4) |
| P(1)-C(21) | 1.809(2) | | |

| | | | |
|---|---|---|---|
| C(11)-Au(1)-C(1) | 175.24(9) | | |
| C(2)-C(1)-P(1) | 116.17(19) | C(12)-C(11)-Au(1) | 123.27(19) |
| C(2)-C(1)-Au(1) | 121.15(19) | F(1)-C(12)-C(13) | 116.4(2) |
| P(1)-C(1)-Au(1) | 122.67(13) | F(1)-C(12)-C(11) | 119.7(2) |
| C(3)-C(2)-C(1) | 178.4(3) | C(13)-C(12)-C(11) | 124.0(2) |
| C(16)-C(11)-C(12) | 113.7(2) | F(2)-C(13)-C(12) | 121.2(2) |
| C(16)-C(11)-Au(1) | 122.87(18) | F(2)-C(13)-C(14) | 119.2(2) |

| | | | |
|---|---|---|---|
| C(12)-C(13)-C(14) | 119.5(2) | C(24)-C(23)-C(22) | 120.3(3) |
| F(3)-C(14)-C(15) | 120.4(2) | C(25)-C(24)-C(23) | 120.1(2) |
| F(3)-C(14)-C(13) | 121.0(2) | C(24)-C(25)-C(26) | 120.3(2) |
| C(15)-C(14)-C(13) | 118.6(2) | C(25)-C(26)-C(21) | 119.9(2) |
| F(4)-C(15)-C(16) | 121.2(2) | C(32)-C(31)-C(36) | 119.5(2) |
| F(4)-C(15)-C(14) | 119.3(2) | C(32)-C(31)-P(1) | 120.86(18) |
| C(16)-C(15)-C(14) | 119.5(2) | C(36)-C(31)-P(1) | 119.61(19) |
| F(5)-C(16)-C(15) | 115.6(2) | C(33)-C(32)-C(31) | 120.2(2) |
| F(5)-C(16)-C(11) | 119.7(2) | C(32)-C(33)-C(34) | 120.1(3) |
| C(15)-C(16)-C(11) | 124.7(2) | C(35)-C(34)-C(33) | 120.0(2) |
| C(1)-P(1)-C(41) | 110.81(12) | C(34)-C(35)-C(36) | 120.3(2) |
| C(1)-P(1)-C(31) | 109.60(11) | C(35)-C(36)-C(31) | 119.8(2) |
| C(41)-P(1)-C(31) | 109.51(11) | C(42)-C(41)-C(46) | 120.2(2) |
| C(1)-P(1)-C(21) | 111.84(11) | C(42)-C(41)-P(1) | 118.30(19) |
| C(41)-P(1)-C(21) | 106.73(11) | C(46)-C(41)-P(1) | 121.46(19) |
| C(31)-P(1)-C(21) | 108.26(11) | C(43)-C(42)-C(41) | 120.1(2) |
| C(26)-C(21)-C(22) | 119.6(2) | C(42)-C(43)-C(44) | 119.9(3) |
| C(26)-C(21)-P(1) | 119.63(19) | C(45)-C(44)-C(43) | 120.0(2) |
| C(22)-C(21)-P(1) | 120.77(19) | C(44)-C(45)-C(46) | 120.8(2) |
| C(23)-C(22)-C(21) | 119.9(2) | C(41)-C(46)-C(45) | 118.9(2) |

**Table S6.** Crystal data and structure refinement for **3**.

| | |
|---|---|
| Identification code | c293 |
| Empirical formula | C40 H32 Au F3 O3 P2 S |
| Formula weight | 908.62 |
| Temperature | 100(2) K |
| Wavelength | 0.71073 A |
| Crystal system, space group | Triclinic, P-1 |
| Unit cell dimensions | a = 7.9063(16) A alpha = 64.53(3) deg. |
| | b = 14.649(3) A beta = 82.11(3) deg. |
| | c = 17.000(3) A gamma = 83.47(3) deg. |
| Volume | 1757.4(6) A^3 |
| Z, Calculated density | 2, 1.717 Mg/m^3 |
| Absorption coefficient | 4.391 mm^-1 |
| F(000) | 896 |
| Crystal size | 0.43 x 0.07 x 0.05 mm |
| Theta range for data collection | 4.25 to 25.50 deg. |
| Limiting indices | -9<=h<=8, -17<=k<=12, -20<=l<=19 |
| Reflections collected / unique | 11238 / 6512 [R(int) = 0.0551] |
| Completeness to theta = 25.50 | 99.4 % |
| Absorption correction | Semi-empirical from equivalents |
| Max. and min. transmission | 0.8103 and 0.2540 |
| Refinement method | Full-matrix least-squares on F^2 |
| Data / restraints / parameters | 6512 / 7 / 459 |
| Goodness-of-fit on F^2 | 1.042 |
| Final R indices [I>2sigma(I)] | R1 = 0.0800, wR2 = 0.1636 |
| R indices (all data) | R1 = 0.1073, wR2 = 0.1821 |
| Largest diff. peak and hole | 4.586 and -3.908 e.A^-3 |

**Table S7.** Bond lengths [A] and angles [deg] for complex **3**.

| | | | |
|---|---|---|---|
| Au(1)-C(1) | 2.063(11) | C(23)-C(24) | 1.37(2) |
| Au(1)-P(1) | 2.265(3) | C(23)-H(23) | 0.9500 |
| C(1)-C(2) | 1.293(16) | C(24)-C(25) | 1.36(2) |
| C(1)-P(2) | 1.758(11) | C(24)-H(24) | 0.9500 |
| C(3)-C(2) | 1.290(19) | C(25)-C(26) | 1.39(2) |
| C(3)-H(1) | 0.92(11) | C(25)-H(25) | 0.9500 |
| C(3)-H(2) | 0.74(10) | C(26)-H(26) | 0.9500 |
| P(1)-C(11) | 1.793(14) | C(31)-C(36) | 1.353(19) |
| P(1)-C(21) | 1.801(14) | C(31)-C(32) | 1.38(2) |
| P(1)-C(31) | 1.806(14) | C(32)-C(33) | 1.40(2) |
| C(11)-C(16) | 1.34(2) | C(32)-H(32) | 0.9500 |
| C(11)-C(12) | 1.381(19) | C(33)-C(34) | 1.35(2) |
| C(12)-C(13) | 1.36(2) | C(33)-H(33) | 0.9500 |
| C(12)-H(12) | 0.9500 | C(34)-C(35) | 1.35(2) |
| C(13)-C(14) | 1.33(2) | C(34)-H(34) | 0.9500 |
| C(13)-H(13) | 0.9500 | C(35)-C(36) | 1.41(2) |
| C(14)-C(15) | 1.38(3) | C(35)-H(35) | 0.9500 |
| C(14)-H(14) | 0.9500 | C(36)-H(36) | 0.9500 |
| C(15)-C(16) | 1.35(3) | P(2)-C(41) | 1.784(12) |
| C(15)-H(15) | 0.9500 | P(2)-C(61) | 1.793(14) |
| C(16)-H(16) | 0.9500 | P(2)-C(51) | 1.808(13) |
| C(21)-C(26) | 1.36(2) | C(41)-C(46) | 1.359(19) |
| C(21)-C(22) | 1.408(18) | C(41)-C(42) | 1.401(18) |
| C(22)-C(23) | 1.39(2) | C(42)-C(43) | 1.377(17) |
| C(22)-H(22) | 0.9500 | | |
| C(42)-H(42) | 0.9500 | C(43)-C(44) | 1.36(2) |

| | | | |
|---|---|---|---|
| C(43)-H(43) | 0.9500 | C(61)-C(62) | 1.404(16) |
| C(44)-C(45) | 1.39(2) | C(62)-C(63) | 1.377(19) |
| C(44)-H(44) | 0.9500 | C(62)-H(62) | 0.9500 |
| C(45)-C(46) | 1.379(19) | C(63)-C(64) | 1.39(2) |
| C(45)-H(45) | 0.9500 | C(63)-H(63) | 0.9500 |
| C(46)-H(46) | 0.9500 | C(64)-C(65) | 1.36(2) |
| C(51)-C(52) | 1.373(17) | C(64)-H(64) | 0.9500 |
| C(51)-C(56) | 1.379(18) | C(65)-C(66) | 1.35(2) |
| C(52)-C(53) | 1.402(19) | C(65)-H(65) | 0.9500 |
| C(52)-H(52) | 0.9500 | C(66)-H(66) | 0.9500 |
| C(53)-C(54) | 1.38(2) | S(1)-O(2) | 1.428(9) |
| C(53)-H(53) | 0.9500 | S(1)-O(3) | 1.501(11) |
| C(54)-C(55) | 1.36(2) | S(1)-O(1) | 1.540(11) |
| C(54)-H(54) | 0.9500 | S(1)-C(70) | 1.636(17) |
| C(55)-C(56) | 1.37(2) | F(1)-C(70) | 1.405(13) |
| C(55)-H(55) | 0.9500 | F(2)-C(70) | 1.393(13) |
| C(56)-H(56) | 0.9500 | F(3)-C(70) | 1.408(14) |
| C(61)-C(66) | 1.390(18) | | |

| | | | |
|---|---|---|---|
| C(1)-Au(1)-P(1) | 177.7(3) | C(11)-P(1)-Au(1) | 114.0(4) |
| C(2)-C(1)-P(2) | 121.1(9) | C(21)-P(1)-Au(1) | 111.3(5) |
| C(2)-C(1)-Au(1) | 119.6(8) | C(31)-P(1)-Au(1) | 110.5(4) |
| P(2)-C(1)-Au(1) | 119.0(6) | C(16)-C(11)-C(12) | 116.5(14) |
| C(2)-C(3)-H(1) | 110(7) | C(16)-C(11)-P(1) | 123.4(12) |
| C(2)-C(3)-H(2) | 120(9) | C(12)-C(11)-P(1) | 119.6(11) |
| H(1)-C(3)-H(2) | 129(10) | C(13)-C(12)-C(11) | 120.8(14) |
| C(11)-P(1)-C(21) | 106.4(6) | C(13)-C(12)-H(12) | 119.6 |
| C(11)-P(1)-C(31) | 106.3(6) | C(11)-C(12)-H(12) | 119.6 |
| C(21)-P(1)-C(31) | 107.9(6) | C(14)-C(13)-C(12) | 121.4(15) |

| | | | |
|---|---|---|---|
| C(14)-C(13)-H(13) | 119.3 | C(36)-C(31)-C(32) | 120.0(14) |
| C(12)-C(13)-H(13) | 119.3 | C(36)-C(31)-P(1) | 123.3(12) |
| C(13)-C(14)-C(15) | 118.1(17) | C(32)-C(31)-P(1) | 116.6(10) |
| C(13)-C(14)-H(14) | 120.9 | C(31)-C(32)-C(33) | 119.6(15) |
| C(15)-C(14)-H(14) | 120.9 | C(31)-C(32)-H(32) | 120.2 |
| C(16)-C(15)-C(14) | 120.0(19) | C(33)-C(32)-H(32) | 120.2 |
| C(16)-C(15)-H(15) | 120.0 | C(34)-C(33)-C(32) | 120.4(16) |
| C(14)-C(15)-H(15) | 120.0 | C(34)-C(33)-H(33) | 119.8 |
| C(11)-C(16)-C(15) | 122.8(17) | C(32)-C(33)-H(33) | 119.8 |
| C(11)-C(16)-H(16) | 118.6 | C(33)-C(34)-C(35) | 119.6(16) |
| C(15)-C(16)-H(16) | 118.6 | C(33)-C(34)-H(34) | 120.2 |
| C(26)-C(21)-C(22) | 119.2(14) | C(35)-C(34)-H(34) | 120.2 |
| C(26)-C(21)-P(1) | 119.9(11) | C(34)-C(35)-C(36) | 121.3(15) |
| C(22)-C(21)-P(1) | 120.9(12) | C(34)-C(35)-H(35) | 119.3 |
| C(23)-C(22)-C(21) | 118.4(15) | C(36)-C(35)-H(35) | 119.3 |
| C(23)-C(22)-H(22) | 120.8 | C(31)-C(36)-C(35) | 118.9(16) |
| C(21)-C(22)-H(22) | 120.8 | C(31)-C(36)-H(36) | 120.5 |
| C(24)-C(23)-C(22) | 121.5(15) | C(35)-C(36)-H(36) | 120.5 |
| C(24)-C(23)-H(23) | 119.2 | C(1)-P(2)-C(41) | 111.1(5) |
| C(22)-C(23)-H(23) | 119.2 | C(1)-P(2)-C(61) | 107.7(6) |
| C(25)-C(24)-C(23) | 119.6(16) | C(41)-P(2)-C(61) | 109.3(6) |
| C(25)-C(24)-H(24) | 120.2 | C(1)-P(2)-C(51) | 112.0(6) |
| C(23)-C(24)-H(24) | 120.2 | C(41)-P(2)-C(51) | 108.9(6) |
| C(24)-C(25)-C(26) | 119.9(17) | C(61)-P(2)-C(51) | 107.8(6) |
| C(24)-C(25)-H(25) | 120.1 | C(46)-C(41)-C(42) | 119.9(12) |
| C(26)-C(25)-H(25) | 120.1 | C(46)-C(41)-P(2) | 121.8(10) |
| C(21)-C(26)-C(25) | 121.5(15) | C(42)-C(41)-P(2) | 118.3(10) |
| C(21)-C(26)-H(26) | 119.3 | C(43)-C(42)-C(41) | 119.2(13) |
| C(25)-C(26)-H(26) | 119.3 | C(43)-C(42)-H(42) | 120.4 |

| | | | |
|---|---|---|---|
| C(41)-C(42)-H(42) | 120.4 | C(55)-C(56)-H(56) | 120.3 |
| C(44)-C(43)-C(42) | 121.0(13) | C(51)-C(56)-H(56) | 120.3 |
| C(44)-C(43)-H(43) | 119.5 | C(66)-C(61)-C(62) | 119.5(13) |
| C(42)-C(43)-H(43) | 119.5 | C(66)-C(61)-P(2) | 120.7(10) |
| C(43)-C(44)-C(45) | 119.5(13) | C(62)-C(61)-P(2) | 119.8(10) |
| C(43)-C(44)-H(44) | 120.2 | C(63)-C(62)-C(61) | 117.9(13) |
| C(45)-C(44)-H(44) | 120.2 | C(63)-C(62)-H(62) | 121.1 |
| C(46)-C(45)-C(44) | 120.0(15) | C(61)-C(62)-H(62) | 121.1 |
| C(46)-C(45)-H(45) | 120.0 | C(62)-C(63)-C(64) | 121.6(12) |
| C(44)-C(45)-H(45) | 120.0 | C(62)-C(63)-H(63) | 119.2 |
| C(41)-C(46)-C(45) | 120.4(14) | C(64)-C(63)-H(63) | 119.2 |
| C(41)-C(46)-H(46) | 119.8 | C(65)-C(64)-C(63) | 119.1(14) |
| C(45)-C(46)-H(46) | 119.8 | C(65)-C(64)-H(64) | 120.4 |
| C(52)-C(51)-C(56) | 120.3(13) | C(63)-C(64)-H(64) | 120.4 |
| C(52)-C(51)-P(2) | 119.4(10) | C(66)-C(65)-C(64) | 121.3(15) |
| C(56)-C(51)-P(2) | 120.1(10) | C(66)-C(65)-H(65) | 119.3 |
| C(51)-C(52)-C(53) | 119.9(13) | C(64)-C(65)-H(65) | 119.3 |
| C(51)-C(52)-H(52) | 120.1 | C(65)-C(66)-C(61) | 120.6(13) |
| C(53)-C(52)-H(52) | 120.1 | C(65)-C(66)-H(66) | 119.7 |
| C(54)-C(53)-C(52) | 119.1(14) | C(61)-C(66)-H(66) | 119.7 |
| C(54)-C(53)-H(53) | 120.5 | O(2)-S(1)-O(3) | 115.4(9) |
| C(52)-C(53)-H(53) | 120.5 | O(2)-S(1)-O(1) | 117.9(10) |
| C(55)-C(54)-C(53) | 119.9(13) | O(3)-S(1)-O(1) | 106.4(11) |
| C(55)-C(54)-H(54) | 120.0 | O(2)-S(1)-C(70) | 110.1(9) |
| C(53)-C(54)-H(54) | 120.0 | O(3)-S(1)-C(70) | 104.9(8) |
| C(54)-C(55)-C(56) | 121.5(13) | O(1)-S(1)-C(70) | 100.4(9) |
| C(54)-C(55)-H(55) | 119.3 | F(2)-C(70)-F(1) | 109.2(12) |
| C(56)-C(55)-H(55) | 119.3 | F(2)-C(70)-F(3) | 111.4(15) |
| C(55)-C(56)-C(51) | 119.3(14) | F(1)-C(70)-F(3) | 123.3(16) |

| | | | |
|---|---|---|---|
| F(2)-C(70)-S(1) | 103.6(13) | F(3)-C(70)-S(1) | 105.4(12) |
| F(1)-C(70)-S(1) | 101.7(12) | C(3)-C(2)-C(1) | 178.6(14) |

**Table S8.** Crystal data and structure refinement for (±)-**5**.

| | |
|---|---|
| Identification code | c285s |
| Empirical formula | $C_{39}$ $H_{17}$ Au $F_{15}$ P |
| Formula weight | 998.46 |
| Temperature | 100(2) K |
| Wavelength | 0.71073 A |
| Crystal system, space group | Monoclinic, P2(1)/c |
| Unit cell dimensions | a = 27.8653(7) A alpha = 90 deg. |
| | b = 10.5925(2) A beta = 106.431(3) deg. |
| | c = 24.5903(8) A gamma = 90 deg. |
| Volume | 6961.7(3) A^3 |
| Z, Calculated density | 8, 1.905 Mg/m^3 |
| Absorption coefficient | 4.383 mm^-1 |
| F(000) | 3840 |
| Crystal size | 0.23 x 0.16 x 0.12 mm |
| Theta range for data collection | 4.14 to 25.50 deg. |
| Limiting indices | -24<=h<=33, -12<=k<=10, -29<=l<=18 |
| Reflections collected / unique | 26742 / 12879 [R(int) = 0.0353] |
| Completeness to theta = 25.50 | 99.4 % |
| Absorption correction | Semi-empirical from equivalents |
| Max. and min. transmission | 0.6213 and 0.4322 |
| Refinement method | Full-matrix least-squares on F^2 |
| Data / restraints / parameters | 12879 / 0 / 1025 |
| Goodness-of-fit on F^2 | 1.067 |
| Final R indices [I>2sigma(I)] | R1 = 0.0433, wR2 = 0.0952 |
| R indices (all data) | R1 = 0.0572, wR2 = 0.1021 |
| Largest diff. peak and hole | 2.952 and -1.874 e.A^-3 |

**Table S9**. Bond lengths [A] and angles [deg] for complex (±)-**5**.

| | | | |
|---|---|---|---|
| Au(1)-C(41) | 2.056(6) | C(34)-C(35) | 1.382(10) |
| Au(1)-C(61) | 2.063(6) | C(35)-C(36) | 1.372(9) |
| Au(1)-C(51) | 2.070(6) | C(41)-C(42) | 1.381(9) |
| Au(1)-C(1) | 2.076(7) | C(41)-C(46) | 1.388(8) |
| C(1)-C(2) | 1.276(9) | C(42)-F(1) | 1.353(7) |
| C(2)-C(3) | 1.322(9) | C(42)-C(43) | 1.376(8) |
| C(3)-P(1) | 1.769(6) | C(43)-F(2) | 1.347(7) |
| P(1)-C(11) | 1.790(6) | C(43)-C(44) | 1.381(9) |
| P(1)-C(21) | 1.792(6) | C(44)-F(3) | 1.341(6) |
| P(1)-C(31) | 1.800(6) | C(44)-C(45) | 1.376(9) |
| C(11)-C(16) | 1.396(9) | C(45)-F(4) | 1.349(7) |
| C(11)-C(12) | 1.407(9) | C(45)-C(46) | 1.380(8) |
| C(12)-C(13) | 1.380(9) | C(46)-F(5) | 1.349(7) |
| C(13)-C(14) | 1.375(10) | C(51)-C(56) | 1.370(9) |
| C(14)-C(15) | 1.385(10) | C(51)-C(52) | 1.381(9) |
| C(15)-C(16) | 1.390(9) | C(52)-F(6) | 1.359(7) |
| C(21)-C(22) | 1.390(8) | C(52)-C(53) | 1.377(9) |
| C(21)-C(26) | 1.397(9) | C(53)-F(7) | 1.351(7) |
| C(22)-C(23) | 1.385(9) | C(53)-C(54) | 1.369(9) |
| C(23)-C(24) | 1.386(9) | C(54)-F(8) | 1.343(7) |
| C(24)-C(25) | 1.384(9) | C(54)-C(55) | 1.375(10) |
| C(25)-C(26) | 1.397(9) | C(55)-F(9) | 1.348(7) |
| C(31)-C(36) | 1.393(9) | C(55)-C(56) | 1.389(9) |
| C(31)-C(32) | 1.408(9) | C(56)-F(10) | 1.357(7) |
| C(32)-C(33) | 1.368(9) | C(61)-C(66) | 1.375(9) |
| C(33)-C(34) | 1.382(10) | C(61)-C(62) | 1.392(9) |

| | | | |
|---|---|---|---|
| C(62)-F(11) | 1.358(7) | C(84)-C(85) | 1.368(11) |
| C(62)-C(63) | 1.380(9) | C(85)-C(86) | 1.391(11) |
| C(63)-F(12) | 1.343(8) | C(91)-C(96) | 1.374(10) |
| C(63)-C(64) | 1.377(10) | C(91)-C(92) | 1.389(9) |
| C(64)-F(13) | 1.353(7) | C(92)-C(93) | 1.410(9) |
| C(64)-C(65) | 1.378(10) | C(93)-C(94) | 1.347(11) |
| C(65)-F(14) | 1.340(8) | C(94)-C(95) | 1.373(11) |
| C(65)-C(66) | 1.388(9) | C(95)-C(96) | 1.381(10) |
| C(66)-F(15) | 1.347(7) | C(101)-C(106) | 1.371(9) |
| Au(2)-C(67) | 2.055(7) | C(101)-C(102) | 1.372(9) |
| Au(2)-C(121) | 2.062(6) | C(102)-F(16) | 1.352(8) |
| Au(2)-C(101) | 2.063(6) | C(102)-C(103) | 1.394(10) |
| Au(2)-C(111) | 2.064(6) | C(103)-F(17) | 1.346(9) |
| C(67)-C(68) | 1.276(9) | C(103)-C(104) | 1.348(12) |
| C(68)-C(69) | 1.322(9) | C(104)-F(18) | 1.351(8) |
| C(69)-P(2) | 1.757(7) | C(104)-C(105) | 1.373(11) |
| P(2)-C(71) | 1.796(7) | C(105)-F(19) | 1.340(9) |
| P(2)-C(91) | 1.800(7) | C(105)-C(106) | 1.397(10) |
| P(2)-C(81) | 1.803(7) | C(106)-F(20) | 1.344(8) |
| C(71)-C(76) | 1.390(10) | C(111)-C(112) | 1.378(9) |
| C(71)-C(72) | 1.402(9) | C(111)-C(116) | 1.381(9) |
| C(72)-C(73) | 1.374(10) | C(112)-F(21) | 1.349(7) |
| C(73)-C(74) | 1.363(10) | C(112)-C(113) | 1.379(9) |
| C(74)-C(75) | 1.365(11) | C(113)-F(22) | 1.349(7) |
| C(75)-C(76) | 1.385(11) | C(113)-C(114) | 1.363(10) |
| C(81)-C(86) | 1.378(10) | C(114)-F(23) | 1.351(7) |
| C(81)-C(82) | 1.392(9) | C(114)-C(115) | 1.389(10) |
| C(82)-C(83) | 1.372(10) | C(115)-F(24) | 1.335(7) |
| C(83)-C(84) | 1.359(11) | C(115)-C(116) | 1.379(9) |

| | | | |
|---|---|---|---|
| C(116)-F(25) | 1.361(7) | C(123)-C(124) | 1.376(10) |
| C(121)-C(126) | 1.361(9) | C(124)-F(28) | 1.331(8) |
| C(121)-C(122) | 1.380(10) | C(124)-C(125) | 1.386(10) |
| C(122)-F(26) | 1.351(8) | C(125)-F(29) | 1.350(8) |
| C(122)-C(123) | 1.376(10) | C(125)-C(126) | 1.382(9) |
| C(123)-F(27) | 1.344(8) | C(126)-F(30) | 1.367(7) |

| | | | |
|---|---|---|---|
| C(41)-Au(1)-C(61) | 177.9(2) | C(15)-C(16)-C(11) | 119.5(6) |
| C(41)-Au(1)-C(51) | 91.8(2) | C(22)-C(21)-C(26) | 119.6(6) |
| C(61)-Au(1)-C(51) | 87.1(2) | C(22)-C(21)-P(1) | 119.5(5) |
| C(41)-Au(1)-C(1) | 87.3(2) | C(26)-C(21)-P(1) | 120.9(5) |
| C(61)-Au(1)-C(1) | 93.9(2) | C(23)-C(22)-C(21) | 120.7(6) |
| C(51)-Au(1)-C(1) | 176.7(2) | C(22)-C(23)-C(24) | 119.5(6) |
| C(2)-C(1)-Au(1) | 123.7(5) | C(25)-C(24)-C(23) | 120.8(6) |
| C(1)-C(2)-C(3) | 176.3(7) | C(24)-C(25)-C(26) | 119.7(6) |
| C(2)-C(3)-P(1) | 119.2(5) | C(25)-C(26)-C(21) | 119.7(6) |
| C(3)-P(1)-C(11) | 107.9(3) | C(36)-C(31)-C(32) | 120.0(6) |
| C(3)-P(1)-C(21) | 109.1(3) | C(36)-C(31)-P(1) | 118.4(5) |
| C(11)-P(1)-C(21) | 110.2(3) | C(32)-C(31)-P(1) | 121.4(5) |
| C(3)-P(1)-C(31) | 111.0(3) | C(33)-C(32)-C(31) | 118.8(6) |
| C(11)-P(1)-C(31) | 110.7(3) | C(32)-C(33)-C(34) | 121.2(7) |
| C(21)-P(1)-C(31) | 107.9(3) | C(35)-C(34)-C(33) | 119.9(7) |
| C(16)-C(11)-C(12) | 120.5(6) | C(36)-C(35)-C(34) | 120.4(7) |
| C(16)-C(11)-P(1) | 118.4(5) | C(35)-C(36)-C(31) | 119.8(7) |
| C(12)-C(11)-P(1) | 120.5(5) | C(42)-C(41)-C(46) | 115.4(5) |
| C(13)-C(12)-C(11) | 118.4(6) | C(42)-C(41)-Au(1) | 121.6(4) |
| C(14)-C(13)-C(12) | 121.4(7) | C(46)-C(41)-Au(1) | 123.0(4) |
| C(13)-C(14)-C(15) | 120.3(6) | F(1)-C(42)-C(43) | 117.4(5) |
| C(14)-C(15)-C(16) | 119.9(6) | F(1)-C(42)-C(41) | 119.3(5) |

| | | | |
|---|---|---|---|
| C(43)-C(42)-C(41) | 123.3(6) | F(10)-C(56)-C(55) | 116.0(6) |
| F(2)-C(43)-C(42) | 121.1(6) | C(51)-C(56)-C(55) | 123.8(6) |
| F(2)-C(43)-C(44) | 119.3(5) | C(66)-C(61)-C(62) | 115.5(6) |
| C(42)-C(43)-C(44) | 119.6(6) | C(66)-C(61)-Au(1) | 122.5(5) |
| F(3)-C(44)-C(45) | 120.7(6) | C(62)-C(61)-Au(1) | 121.8(5) |
| F(3)-C(44)-C(43) | 120.3(5) | F(11)-C(62)-C(63) | 117.0(6) |
| C(45)-C(44)-C(43) | 119.1(5) | F(11)-C(62)-C(61) | 119.7(5) |
| F(4)-C(45)-C(44) | 119.4(5) | C(63)-C(62)-C(61) | 123.3(6) |
| F(4)-C(45)-C(46) | 120.8(5) | F(12)-C(63)-C(64) | 120.0(6) |
| C(44)-C(45)-C(46) | 119.8(5) | F(12)-C(63)-C(62) | 120.9(6) |
| F(5)-C(46)-C(45) | 117.2(5) | C(64)-C(63)-C(62) | 119.0(6) |
| F(5)-C(46)-C(41) | 119.9(5) | F(13)-C(64)-C(63) | 120.5(6) |
| C(45)-C(46)-C(41) | 122.8(6) | F(13)-C(64)-C(65) | 119.8(6) |
| C(56)-C(51)-C(52) | 114.8(6) | C(63)-C(64)-C(65) | 119.8(6) |
| C(56)-C(51)-Au(1) | 120.7(4) | F(14)-C(65)-C(64) | 120.0(6) |
| C(52)-C(51)-Au(1) | 124.5(5) | F(14)-C(65)-C(66) | 120.7(6) |
| F(6)-C(52)-C(53) | 117.3(6) | C(64)-C(65)-C(66) | 119.4(6) |
| F(6)-C(52)-C(51) | 119.3(5) | F(15)-C(66)-C(61) | 120.1(6) |
| C(53)-C(52)-C(51) | 123.4(6) | F(15)-C(66)-C(65) | 116.9(6) |
| F(7)-C(53)-C(54) | 119.7(6) | C(61)-C(66)-C(65) | 123.0(6) |
| F(7)-C(53)-C(52) | 120.5(6) | C(67)-Au(2)-C(121) | 87.1(3) |
| C(54)-C(53)-C(52) | 119.8(6) | C(67)-Au(2)-C(101) | 90.8(3) |
| F(8)-C(54)-C(53) | 120.4(6) | C(121)-Au(2)-C(101) | 177.4(2) |
| F(8)-C(54)-C(55) | 120.4(6) | C(67)-Au(2)-C(111) | 175.7(3) |
| C(53)-C(54)-C(55) | 119.2(6) | C(121)-Au(2)-C(111) | 88.9(2) |
| F(9)-C(55)-C(54) | 119.6(6) | C(101)-Au(2)-C(111) | 93.3(2) |
| F(9)-C(55)-C(56) | 121.4(6) | C(68)-C(67)-Au(2) | 130.6(6) |
| C(54)-C(55)-C(56) | 119.0(6) | C(67)-C(68)-C(69) | 177.8(7) |
| F(10)-C(56)-C(51) | 120.2(5) | C(68)-C(69)-P(2) | 122.1(5) |

| | |
|---|---|
| C(69)-P(2)-C(71) | 110.3(3) |
| C(69)-P(2)-C(91) | 110.3(3) |
| C(71)-P(2)-C(91) | 108.2(3) |
| C(69)-P(2)-C(81) | 107.1(3) |
| C(71)-P(2)-C(81) | 111.1(3) |
| C(91)-P(2)-C(81) | 109.9(3) |
| C(76)-C(71)-C(72) | 118.5(6) |
| C(76)-C(71)-P(2) | 120.2(5) |
| C(72)-C(71)-P(2) | 121.3(5) |
| C(73)-C(72)-C(71) | 120.4(7) |
| C(74)-C(73)-C(72) | 119.6(7) |
| C(73)-C(74)-C(75) | 121.8(7) |
| C(74)-C(75)-C(76) | 119.3(7) |
| C(75)-C(76)-C(71) | 120.4(7) |
| C(86)-C(81)-C(82) | 118.8(6) |
| C(86)-C(81)-P(2) | 121.0(5) |
| C(82)-C(81)-P(2) | 120.1(5) |
| C(83)-C(82)-C(81) | 119.8(7) |
| C(84)-C(83)-C(82) | 121.4(7) |
| C(83)-C(84)-C(85) | 119.4(7) |
| C(84)-C(85)-C(86) | 120.4(7) |
| C(81)-C(86)-C(85) | 120.1(7) |
| C(96)-C(91)-C(92) | 120.2(7) |
| C(96)-C(91)-P(2) | 120.8(5) |
| C(92)-C(91)-P(2) | 119.1(5) |
| C(91)-C(92)-C(93) | 118.6(7) |
| C(94)-C(93)-C(92) | 120.5(7) |
| C(93)-C(94)-C(95) | 120.6(7) |
| C(94)-C(95)-C(96) | 120.2(7) |
| C(91)-C(96)-C(95) | 120.0(7) |
| C(106)-C(101)-C(102) | 115.3(6) |
| C(106)-C(101)-Au(2) | 122.5(5) |
| C(102)-C(101)-Au(2) | 122.0(5) |
| F(16)-C(102)-C(101) | 119.6(6) |
| F(16)-C(102)-C(103) | 117.0(6) |
| C(101)-C(102)-C(103) | 123.3(7) |
| F(17)-C(103)-C(104) | 120.4(7) |
| F(17)-C(103)-C(102) | 120.4(7) |
| C(104)-C(103)-C(102) | 119.2(7) |
| C(103)-C(104)-F(18) | 120.8(8) |
| C(103)-C(104)-C(105) | 120.2(7) |
| F(18)-C(104)-C(105) | 119.0(8) |
| F(19)-C(105)-C(104) | 121.1(7) |
| F(19)-C(105)-C(106) | 120.1(8) |
| C(104)-C(105)-C(106) | 118.8(7) |
| F(20)-C(106)-C(101) | 119.3(6) |
| F(20)-C(106)-C(105) | 117.7(6) |
| C(101)-C(106)-C(105) | 123.0(7) |
| C(112)-C(111)-C(116) | 115.9(6) |
| C(112)-C(111)-Au(2) | 123.0(5) |
| C(116)-C(111)-Au(2) | 121.0(5) |
| F(21)-C(112)-C(111) | 120.1(6) |
| F(21)-C(112)-C(113) | 117.4(6) |
| C(111)-C(112)-C(113) | 122.5(6) |
| F(22)-C(113)-C(114) | 119.3(6) |
| F(22)-C(113)-C(112) | 120.7(6) |
| C(114)-C(113)-C(112) | 120.0(6) |
| F(23)-C(114)-C(113) | 120.6(6) |

| | |
|---|---|
| F(23)-C(114)-C(115) | 119.6(6) |
| C(113)-C(114)-C(115) | 119.8(6) |
| F(24)-C(115)-C(116) | 121.3(6) |
| F(24)-C(115)-C(114) | 120.2(6) |
| C(116)-C(115)-C(114) | 118.5(6) |
| C(122)-C(121)-Au(2) | 122.8(5) |
| F(26)-C(122)-C(123) | 117.6(6) |
| F(26)-C(122)-C(121) | 119.7(6) |
| C(123)-C(122)-C(121) | 122.6(7) |
| F(27)-C(123)-C(122) | 121.2(6) |
| F(27)-C(123)-C(124) | 118.7(6) |
| C(122)-C(123)-C(124) | 120.0(6) |
| F(28)-C(124)-C(123) | 119.8(6) |
| F(28)-C(124)-C(125) | 121.5(6) |
| C(123)-C(124)-C(125) | 118.7(6) |
| F(29)-C(125)-C(126) | 120.9(6) |
| F(29)-C(125)-C(124) | 120.0(6) |
| C(126)-C(125)-C(124) | 119.1(6) |
| C(121)-C(126)-F(30) | 120.5(6) |
| C(121)-C(126)-C(125) | 123.4(6) |
| F(30)-C(126)-C(125) | 116.1(6) |
| F(25)-C(116)-C(115) | 116.9(6) |
| F(25)-C(116)-C(111) | 119.8(6) |
| C(115)-C(116)-C(111) | 123.3(6) |
| C(126)-C(121)-C(122) | 116.0(6) |
| C(126)-C(121)-Au(2) | 121.0(5) |