Supporting information

Ligand Effects in Gold- and Platinum-Catalyzed Cyclization of Enynes: Chiral Gold Complexes for the Enantioselective Alkoxycyclization

M. Paz Muñoz, Javier Adrio, Juan Carlos Carretero, and Antonio M. Echavarren*

Departamento de Química Orgánica, Universidad Autónoma de Madrid, Cantoblanco, 28049 Madrid, and Institute of Chemical Research of Catalonia (ICIQ), 43007 Tarragona, Spain

General Procedure for Asymmetric Alkoxycyclization of Enynes.

$PtCl_2$-catalyzed reaction: A mixture of enyne (0.12 mmol), the chiral ligand (5-10 mol%), and $PtCl_2$ (5 mol%) in MeOH (5 mL) was heated under reflux for the stated time. The solvent was evaporated, and the crude mixture was purified by flash chromatography (hexane-EtOAc mixtures) to give the corresponding carbocycles.

[Au(L^*)Cl]-catalyzed reaction: A mixture of [Au(L^*)Cl] (2 mol%) or [$L^*(AuCl)_2$] (1.6 mol%), and $AgSbF_6$ (2 mol%) in MeOH (1 mL) was stirred at room temperature for 5 min. The enyne (0.12 mmol) was added in MeOH (2 mL) and the reaction mixture was stirred at room temperature for the stated time. The mixture was filtered through SiO_2, and the solvent was evaporated. The crude mixture was purified by flash chromatography (hexane-EtOAc mixtures) to give the carbocycles.

The enantiomeric excesses were determined at 25°C in *Perkin-Elmer Integral 4000* or *Agilent 1100 Series* HPLC apparatus. The chiral column and conditions were detailed in each case.

Racemic **8**, **9**, **17**, **18**, **32**, **51**, **53**, **55** and **56** have been described before.[1]

Dimethyl-3-(1-methoxy-1-methylethyl)-4-methylenecyclopentane 1,1-dicarboxylate (8). Chiral Column: *Daicel ChiralPack AD*; Conditions: 95:5 hexane-*i*-PrOH, flow = 0.5 mL/min; λ = 220 nm. Retention times: 9.8 min, and 11.4 min.

1,1-Bis(phenylsulfonyl)-3-(1-methoxy-1-methylethyl)-4-methylenecyclopentane (32). Chiral Column: *Daicel ChiralPack AD*; Conditions: 90:10 hexane-*i*-PrOH, flow = 0.7 mL/min; λ = 220 nm. Retention times: 29.8 min, and 35.4 min. 53% ee: $[\alpha]^{25}$ = +21.2 (c =0.4, $CHCl_3$).

1,1-Bis(phenylsulfonyl)-(3*R)-[(1*S**)-1-(methoxy)phenylmethyl]-4-methylenecyclopentane (17).** Chiral Column: *Daicel ChiralPack AD*; Conditions: 90:10 hexane-*i*-PrOH, flow = 0.7 mL/min; λ = 220 nm. Retention times: 35.2 min, and 38.4 min. 49% ee: $[\alpha]^{25}$ = +21.3 (c =0.3, $CHCl_3$).

1,1-Bis(phenylsulfonyl)-(3*R)-[(1*S**)-1-(allyloxy)phenylmethyl]-4-methylenecyclopentane (51).** Chiral Column: *Daicel ChiralPack AD*; Conditions: 90:10 hexane-*i*-PrOH, flow = 0.7 mL/min; λ = 220 nm. Retention times: 27.9 min, and 29.7 min. 36% ee: $[\alpha]^{25}$ = +8.5 (c =0.2, $CHCl_3$).

(*Z*)-1,1-Bis(phenylsulfonyl)-3-benzylidene-4-(1-methoxy-1-methylethyl)cyclopentane (53). Chiral Column: *Daicel ChiralPack AS*; Conditions: 90:10 hexane-*i*-PrOH, flow = 1 mL/min; λ = 220 nm. Retention times: 14.4 min, and 18.9 min. 94% ee: $[\alpha]^{25}$ = -75.3 (c =0.6, $CHCl_3$).

Dimethyl 3-methyl-3-methoxy-5-methylenecyclohexane-1,1-dicarboxylate (55). Chiral Column: *Daicel ChiralPack AD*; Conditions: 99:1 hexane-*i*-PrOH, flow = 0.7 mL/min; λ = 220 nm. Retention times: 13.8 min, and 15.2 min. 38% ee: $[\alpha]^{25}$ = +7.7 (c =0.6, $CHCl_3$).

Pd-catalyzed deallylation of 51 (Eq 1)

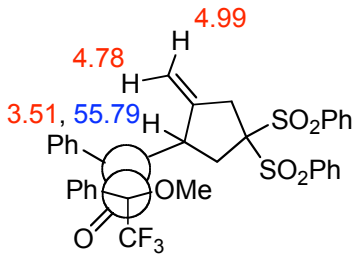
To a solution of **51** (95 mg, 0.19 mmol) in HOAc (1.5 mL) and water (2 drops) at room temperature were added $PdCl_2$ (85 mg, 0.48 mmol) and NaOAc (86 mg, 1.05 mmol). The mixture was then heated at 50°C for 20 h. After being cooled to room temperature, the mixture was filtered through Celtite and washed with Et_2O. The solution was then washed with $NaHCO_3$, and evaporated. After flash chromatography (5:1 hexane-EtOAc,), alcohol **56** was obtained as a white solid (49 mg, 57%).

Formation of Mosher eters of 56

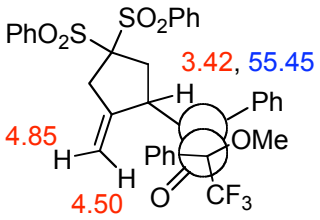
A solution of **56** (49 mg, 0.10 mmol) and (*R*)-(-)-MTPACl (40 mg, 0.15 mmol) was stirred in piridine (0.7 mL) for 2 h. After extractive work-up (Et_2O-10% aqueous HCl) and chromatography (10:1 hexane-EtOAc,), the Mosher esters were obtained as a 2.1:1 mixture (41 mg, 60%).

Determination of the Configuration of 56

Selected ^1H- and ^{13}C-NMR shifts for the Mosher esters of **56** are given below:

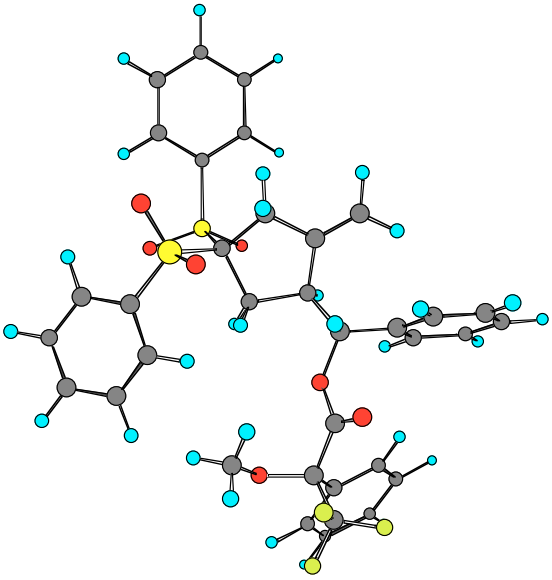


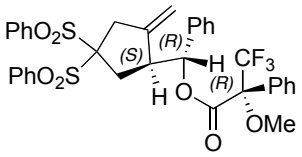
major isomer



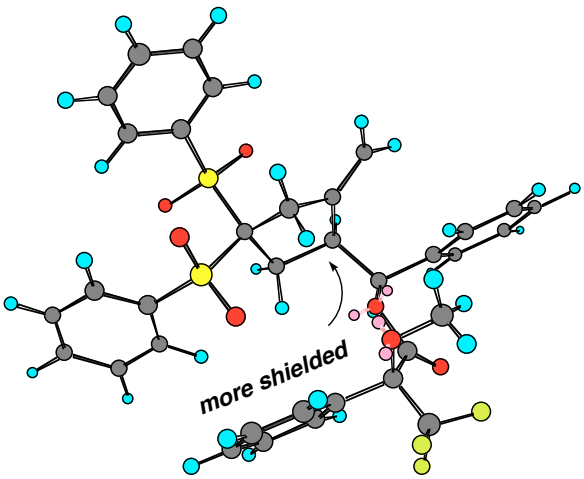
minor isomer

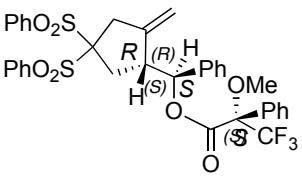
Analysis of the more stable conformations (MM2 + PM3 calculations) in which C(1')H, the carbonyl group, and the CF_3 substituent are in the approximately in the plane, indicates that the minor isomer should show the H at C-4 shielded by the phenyl group pf the MTPA.





major isomer

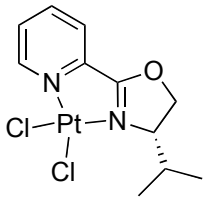




minor isomer

Synthesis of Chiral Metal Complexes

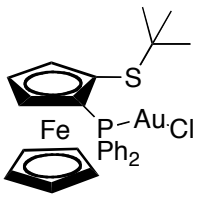
Dichloro-[(*S*)-(-)-4-isopropyl-2-(2-pyridinyl)-2-oxazoline]platinum(II) (30)



A suspension of (*S*)-(-)-4-isopropyl-2-(2-pyridinyl)-2-oxazoline[2] (71 mg, 0.38 mmol) and $PtCl_2$ (100 mg, 0.38 mmol) was stirred in MeOH (10 mL) under reflux for 24 h. The reaction mixture was cooled to room temperature and the solvent was evaporated. The crude was triturated with Et_2O at - 20°C to give complex **30** as an orange solid (85 mg, 49%): ^{1}H NMR ($CDCl_3$, 300 MHz) δ 9.26 (d, J = 5.45 Hz, 1H), 8.15 (t, J = 7.7 Hz, 1H), 7.75 (d, J = 7.7 Hz, 1H), 7.57 (m, 1H), 5.12 (t, J = 9.3 Hz, 1H), 4.82 (dd, J = 8.7, 4.8 Hz, 1H), 4.74 (m, 1H), 2.95 (qd, J = 6.9, 3.0 Hz, 1H), 0.96 (d, J = 7.1 Hz, 3H), 0.80 (d, J = 6.9 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$; DEPT) δ 172.90 (C), 149.01 (CH), 144.80 (C), 139.14 (CH), 129.18 (CH), 126.29 (CH), 73.03 (CH_2), 67.96 (CH), 28.71 (CH), 18.65 (CH_3), 13.81 (CH_3); Anal. Calcd for $C_{11}H_{14}Cl_2N_2OPt{\cdot}H_2O$: C, 27.86; H, 3.40; N, 5.91. Found: C, 28.02; H, 3.45; N, 6.01. HRMS-EI Calcd for $C_{11}H_{14}Cl_2N_2OPt$: 456.0209 (M^+ + 1). Found: 456.0217.

General procedure for the synthesis of chiral Au(I) complexes: To a solution of $Na[AuCl_4]{\cdot}H_2O$ (0.05-0.22 mmol) in H_2O (2-7 mL) at 0°C, was added 2,2'-thiodiethanol (0.05-0.22 mmol) over 15 min. After stirring for 1 h, the ligand (0.15-0.44 mmol) was added in $CHCl_3$ (0.5-2 mL) at 0°C, and the resulting mixture was stirred for a 1 h. After extractive work-up ($CHCl_3$) and trituration (hexane) corresponding Au(I) complexes are obtained.

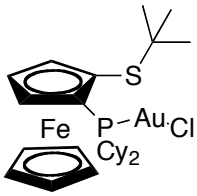
Chloro-(*R*)-2-(tert-Butylsulfenyl)-1-(diphenylphosphino)ferrocene gold(I) (39)



Yellow solid (96%): mp > 190 °C (dec); $[\alpha]^{25}$ = - 103 (c = 1, $CHCl_3$); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.86 (ddd, $^3J(^1H\text{-}^{31}P)$ = 13.3, $J(^1H\text{-}^1H)$ = 7.7, 1.2 Hz, 2H), 7.56 (ddd, $^3J(^1H\text{-}^{31}P)$ = 13.1, $J(^1H\text{-}^1H)$ = 7.7, 1.2 Hz, 2H), 7.50 (t, J = 7.5 Hz, 3H), 7.39-7.33 (m, 3H), 4.84 (quint, J =

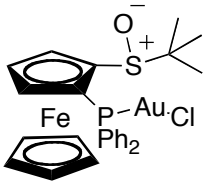
1.0 Hz, 1H), 4.63 (t, J = 2.5 Hz, 1H), 4.28 (q, J = 1.2 Hz, 1H), 4.07 (s, 5H), 1.01 (s, 9H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 134.78 (d, $J(^{13}C\text{-}^{31}P)$ = 14.6 Hz, PPh_2), 133.11 (d, $J(^{13}C\text{-}^{31}P)$ = 14.6 Hz, PPh_2), 132.40, 131.71 (d, $J(^{13}C\text{-}^{31}P)$ = 2.1 Hz, PPh_2), 131.58 (d, $J(^{13}C\text{-}^{31}P)$ = 10.5 Hz, PPh_2), 131.08 (d, $J(^{13}C\text{-}^{31}P)$ = 2.1 Hz, PPh_2), 130.59, 128.71 (d, $J(^{13}C\text{-}^{31}P)$ = 11.5 Hz, PPh_2), 128.65 (d, $J(^{13}C\text{-}^{31}P)$ = 12.5 Hz, PPh_2), 81.96 (d, $J(^{13}C\text{-}^{31}P)$ = 6.3 Hz), 74.10 (d, $J(^{13}C\text{-}^{31}P)$ = 5.2 Hz), 71.71, 71.69, 47.46, 30.98; ^{31}P NMR (300 MHz, $CDCl_3$) δ 22.40 (s). HRMS-TOF-ES-MS Calcd for $C_{26}H_{27}AuClFePS$: 690.0275 (M^+). Found: 690.0241. Anal. Calcd for $C_{26}H_{27}AuClFePS{\cdot}H_2O$: C, 44.06; H, 4.12. Found: C, 44.46; H, 3.90.

Chloro-(*R*)-2-(*tert*-Butylsulfenyl)-1-(dicyclohexylphosphino)ferrocene gold(I) (40)



Orange solid: mp 82-83 ^{o}C; $[\alpha]^{25}$ = + 75.8 (c = 0.53, $CHCl_3$); ^{1}H NMR (300 MHz, $CDCl_3$) δ 4.84 (q, J = 1.2 Hz, 1H), 4.57 (td, J = 2.6, 1.0 Hz, 1H), 4.51 (td, J = 3.0, 1.5 Hz, 1H), 4.32 (s, 5H), 2.6 (m, 1H), 2.30 (m, 1H), 2.10 (m, 4H), 1.85 (m, 4H), 1.72 (m, 1H), 1.57-1.55 (m, 6H), 1.35-1.29 (m, 5H), 1.30 (s, 9H); ^{13}C NMR (75 MHz, $CDCl_3$; DEPT) δ 81.97 (C), 79.47 (d, $J(^{13}C\text{-}^{31}P)$ = 5.6 Hz, CH), 72.66 (C), 71.84 (CH), 47.17 (C), 37.00 (d, $J(^{13}C\text{-}^{31}P)$ = 33.5 Hz), 36.10 (d, $J(^{13}C\text{-}^{31}P)$ = 35.0 Hz), 33.61 (m, CH_2), 31.88 (CH), 31.31 (CH_3), 31.20 (CH), 29.26 (CH_2), 27.20 (CH_2), 27.00 (CH_2), 26.91 (CH_2), 26.74 (CH_2), 26.67 (CH_2), 26.57 (CH_2), 25.64 (CH_2); ^{31}P NMR (121.5 MHz, $CDCl_3$) δ 44.85 (s). HRMS-TOF-ES-MS Calcd for $C_{26}H_{39}AuClFePS$: 702.1214 (M^+). Found: 702.1186.

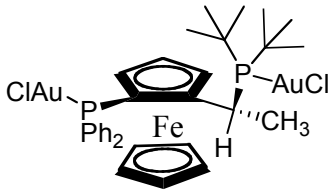
Chloro-(R_{Fc},R_S)-1-(*tert*-Butylsulfinyl)-2-(diphenylphosphino)-ferrocene gold(I) (41)



Orange solid: mp > 190 ^{o}C (dec); $[\alpha]^{25}$ = - 83.2 (c = 0.40, $CHCl_3$); ^{1}H NMR (300 MHz,

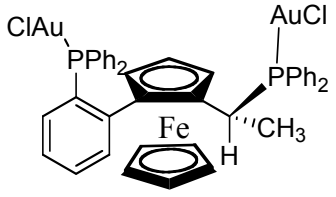
$CDCl_3$) δ 7.80 (ddd, $^3J(^1H\text{-}^{31}P)$ = 13.3, $J(^1H\text{-}^1H)$ = 5.3, 1.6 Hz, 2H), 7.60 (ddd, $^3J(^1H\text{-}^{31}P)$ = 13.3, $J(^1H\text{-}^1H)$ = 7.7, 1.2 Hz, 2H), 7.54-7.35 (m, 6H), 4.78 (q, J = 1.6 Hz, 1H), 4.64 (t, J = 2.6 Hz, 1H), 4.46 (s, 5H), 4.03 (td, J = 2.8, 1.6 Hz, 1H), 1.08 (s, 9H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 134.95 (d, $J(^{13}C\text{-}^{31}P)$ = 15.7 Hz, PPh_2), 133.79 (d, $J(^{13}C\text{-}^{31}P)$ = 14.6 Hz, PPh_2), 131.62 (d, $J(^{13}C\text{-}^{31}P)$ = 12.5 Hz, PPh_2), 130.69 (d, $J(^{13}C\text{-}^{31}P)$ = 20.9 Hz, PPh_2), 128.76, 128.62 (d, $J(^{13}C\text{-}^{31}P)$ = 8.1 Hz, PPh_2), 75.96 (d, $J(^{13}C\text{-}^{31}P)$ = 4.2 Hz), 73.67 (d, $J(^{13}C\text{-}^{31}P)$ = 6.3 Hz), 72.80 (d, $J(^{13}C\text{-}^{31}P)$ = 6.3 Hz), 72.65, 71.78, 57.23, 23.84; ^{31}P NMR (300 MHz, $CDCl_3$) δ 27.43 (s). HRMS-TOF-ES-MS Calcd for $C_{26}H_{27}AuClFePS{\cdot}Na$: 729.0121 ($M^+$). Found: 729.0092.

Gold(I)-complex 42



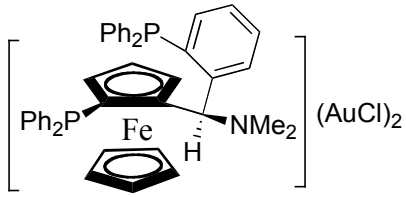
Yellow solid: mp > 200 °C (dec); $[\alpha]^{25}$ = -36.7 (c = 0.63, $CHCl_3$); ^1H NMR (300 MHz, $CDCl_3$) δ 7.81 (dd, $^3J(^1H\text{-}^{31}P)$ = 12.5, $J(^1H\text{-}^1H)$ = 7.3 Hz, 2H), 7.70 (dd, $^3J(^1H\text{-}^{31}P)$ = 12.5, $J(^1H\text{-}^1H)$ = 7.3 Hz, 2H), 7.53-7.40 (m, 6H), 4.80 (br s, 1H), 4.66 (br s, 1H), 4.17 (br s, 1H), 4.10 (s, 5H), 2.13 (dd, $^3J(^1H\text{-}^{31}P)$ = 10.7, $J(^1H\text{-}^1H)$ = 7.7 Hz, 1H), 1.55 (d, $^3J(^1H\text{-}^{31}P)$ = 14.8 Hz, 9H + 3H), 1.01 (d, $^3J(^1H\text{-}^{31}P)$ = 14.8 Hz, 9H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 135.32 (d, $^2J(^{13}C\text{-}^{31}P)$ = 15.7 Hz, PPh_2), 133.60 (d, $^2J(^{13}C\text{-}^{31}P)$ = 14.6 Hz, PPh_2), 131.91, 131.30, 129.70 (d, $^3J(^{13}C\text{-}^{31}P)$ = 11.5 Hz, PPh_2), 128.85 (d, $^3J(^{13}C\text{-}^{31}P)$ = 11.5 Hz, PPh_2), 77.19, 76.09, 75.66, 72.18 (d, $J(^{13}C\text{-}^{31}P)$ = 5.2 Hz), 71.70 (d, $J(^{13}C\text{-}^{31}P)$ = 7.3 Hz), 70.68, 38.45 (d, $J(^{13}C\text{-}^{31}P)$ = 17.8 Hz), 37.70 (d, $J(^{13}C\text{-}^{31}P)$ = 23.0 Hz), 31.89 (d, $J(^{13}C\text{-}^{31}P)$ = 5.2 Hz), 30.97 (br s), 29.44 (d, $J(^{13}C\text{-}^{31}P)$ = 5.2 Hz), 23.94 (br s); ^{31}P NMR (121.5 MHz, $CDCl_3$) δ 87.47 (s), 87.35 (s). Anal. Calcd for $C_{32}H_{40}Au_2Cl_2Fe_2P_2$: C, 38.16; H, 4.00. Found: C, 38.65; H, 4.08.

Gold(I)-complex 43



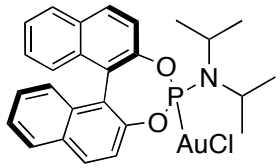
Orange solid: mp > 200 °C; $[\alpha]^{25}$ = - 107.3 (c = 0.30, $CHCl_3$); ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.35 (dd, J = 6.9, 5.1 Hz, 1H), 7.74 (t, J = 7.6 Hz, 1H), 7.57-7.29 (m, 21 H), 6.68 (dd, J = 12.5 , 7.6 Hz, 1H), 4.23 (t, J = 2.6 Hz, 1H), 4.05 (m, 1H), 3.99 (s, 1H), 3.98 (s, 5H), 3.95 (s, 1H), 1.7 (dd, J = 17.4, 7.1 Hz, 3); ^{13}C NMR (75 MHz, $CDCl_3$) δ 135.84 (d, J(^{13}C-^{31}P) = 14.6 Hz), 135.18, 135.05, 134.93, 134.88, 134.70, 134.46 (d, J(^{13}C-^{31}P) = 12.5 Hz), 133.51 (d, J(^{13}C-^{31}P) = 13.6 Hz), 131.74, 131.63, 130.83, 129.68, 129.35 (d, J(^{13}C-^{31}P) = 11.5 Hz), 129.01, 128.87, 128.72, 126.5 (d, J(^{13}C-^{31}P) = 10.0 Hz), 70.57, 70.14, 70.08, 69.98, 67.78; ^{31}P NMR (121.5 MHz, $CDCl_3$) δ 45.15 (s), 26.05 (s). HRMS-TOF-ES-MS Calcd for $C_{42}H_{36}Au_2Cl_2FeP_2$: 1122.0350 ($M^+$). Found: 1122.03090. Anal Calcd for $C_{42}H_{36}Au_2Cl_2FeP_2 \cdot 2H_2O$: C, 43.51; H, 3.48. Found: C, 43.64; H, 3.31.

Gold(I)-complexes 44



Orange solid: mp = 167-168°C; $[\alpha]^{25}$ = + 128.4 (c = 0.50, $CHCl_3$); ^{31}P NMR (300 MHz, $CDCl_3$) δ 31.35 (d, J = 310.8 Hz, part A AB system), 27.30 (d, J = 313.9 Hz, part B AB system), 24.90 (br s), 23.25 (s). MALDI-TOF-MS: *m/z*: 1115.9 (M^+ - Cl), 884.1 (M^+ - $AuCl_2$).

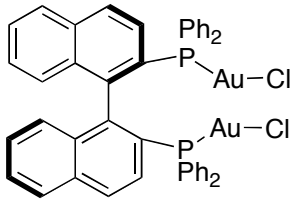
Chloro [*O*,*O*'-(R)-(1,1'-dinaphtyl-2,2'-diyl)-*N*,*N*-di-i-propyl-phosphoramidite] gold(I) (45)



White solid: mp > 200°C; $[\alpha]^{25}$ = - 258.8 (c = 0.50, $CHCl_3$); ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.07 (d, J = 8.5 Hz, 1H), 8.00-7.94 (m, 3H), 7.26 (d, J = 8.9 Hz, 1H), 7.52-7.22 (m, 7H), 3.63 (dq, J = 17.0, 7.3 Hz, 2H), 1.40 (d, J = 6.9 Hz, 3H), 1.29 (d, J = 6.4 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 147.84, 147.23 (d, J(^{13}C-^{31}P) = 6.3 Hz), 132.42-131.24 (d, J(^{13}C-^{31}P) = 87.8 Hz), 132.05, 131.80-130.52 (d, J(^{13}C-^{31}P) = 96.2 Hz), 128.53 (d, J(^{13}C-^{31}P) = 23.0 Hz), 127.00 (d, J(^{13}C-^{31}P) = 20.9 Hz), 126.72, 125.73 (d, J(^{13}C-^{31}P) = 14.6 Hz), 121.00 (d, J(^{13}C-^{31}P) = 43.9 Hz), 47.80 (d, J(^{13}C-^{31}P) = 8.4 Hz), 24.00 (d, J(^{13}C-^{31}P) = 4.2 Hz), 23.67 (d, J(^{13}C-

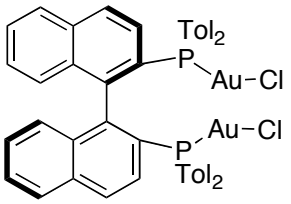
^{31}P) = 4.2 Hz); ^{31}P NMR (300 MHz, $CDCl_3$) δ 127.39 (s). Anal. Calcd for $C_{26}H_{26}AuClNO_2P$: C, 48.20; H, 4.04; N, 2.16. Found: C, 48.15; H, 4.09; N, 2.13.

Gold(I)-complex (46)



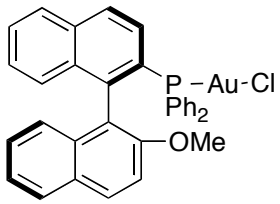
White solid: mp > 200 ^{o}C (dec); $[\alpha]^{25}$ = -16 (c = 0.20, $CHCl_3$); ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.20 (d, J = 8.7 Hz, 2H), 7,96 (d, J = 8.1 Hz, 2H), 7.26-7.32 (m, 17H), 7.31-7.28 (m, 7H), 6.87 (t, J = 7.9 Hz, 2H), 6.67 (d, J = 8.5 Hz, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 134.73 (d, J(^{13}C-^{31}P) = 13.7 Hz), 134.22 (d, J(^{13}C-^{31}P) = 14.7 Hz), 133.90 (d, J(^{13}C-^{31}P) = 10.5 Hz), 132.97, 131.40 (d, J(^{13}C-^{31}P) = 6.3 Hz), 131.38 (d, J(^{13}C-^{31}P) = 5.2 Hz), 130.88, 129.90 (d, J(^{13}C-^{31}P) = 13.6 Hz), 129.90 (d, J(^{13}C-^{31}P) = 11.5 Hz), 128.60 (d, J(^{13}C-^{31}P) = 21.9 Hz), 128.12, 127.29, 126.92 (d, J(^{13}C-^{31}P) = 10.5 Hz), 126.90, 126.05. MALDI-TOF-MS: *m/z*: 1051.0 (M^+ - Cl).

Gold(I)-complex 47



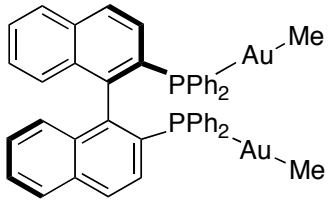
White solid: mp > 200 ^{o}C (dec); $[\alpha]^{25}$ = - 53.5 (c = 0.40, $CHCl_3$); ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.16 (d, J = 8.9 Hz, 2H), 7.96 (d, J = 8.1 Hz, 2H), 7.51-7.39 (m, 8H), 7.10-6.96 (m, 14H), 6.74 (d, J = 8.5 Hz, 2H), 2.33 (s, 12H); ^{13}C NMR (75 MHz, $CDCl_3$, DEPT) δ 141.70 (m, C), 134.61 (d, J(^{13}C-^{31}P) = 14.1 Hz, CH), 133.99 (C), 133.77 (d, J(^{13}C-^{31}P) = 14.5 Hz, CH), 129.85 (CH), 129.72 (CH), 129.62 (CH), 129.45 (d, J(^{13}C-^{31}P) = 1.8 Hz, CH), 128.71 (CH), 128.26 (CH), 128.06 (C), 127.22 (C), 126.85 (d, J(^{13}C-^{31}P) = 4.2 Hz, CH), 126.56 (C), 124.39 (C), 123.54 (C), 21.33 (CH_3); ^{31}P NMR (121.5 MHz, $CDCl_3$) δ 22.23 (s). Anal. Calcd for $C_{48}H_{40}Au_2Cl_2P_2$: C, 50.41; H, 3.53. Found: C, 50.55; H, 3.69.

Chloro [(*R*)-2-methoxy-2'-diphenylphosphino-1,1'-binaphtyl] gold(I) (48)



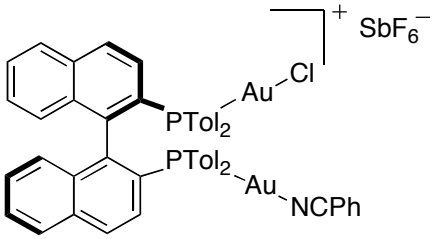
White solid: mp 162-165 °C; $[\alpha]^{25}$ = + 9.4 (c = 0.80, $CHCl_3$); ^1H NMR (300 MHz, $CDCl_3$) δ 8.13 (d, J = 9.1 Hz, 1H), 7.93 (d, J = 8.5 Hz, 2H), 7.87 (d, J = 8.3 Hz, 1H), 7.57-7.19 (m, 16H), 6.95 (t, J = 8.1 Hz, 1H), 6.55 (d, J = 8.5 Hz, 1H), 3.43 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 154.88, 143.89, 134.51 (br s), 134.21 (d, $J(^{13}C\text{-}^{31}P)$ = 14.6 Hz), 133.73, 133.57 (d, $J(^{13}C\text{-}^{31}P)$ = 10.4 Hz), 131.33, 131.18 (dd, $J(^{13}C\text{-}^{31}P)$ = 6.3, 2.1 Hz), 130.30 (d, $J(^{13}C\text{-}^{31}P)$ = 8.4 Hz), 129.50 (d, $J(^{13}C\text{-}^{31}P)$ = 8.4 Hz), 128.97, 128.85 (d, $J(^{13}C\text{-}^{31}P)$ = 3.1 Hz), 128.78, 128.70 (d, $J(^{13}C\text{-}^{31}P)$ = 3.1 Hz), 128.55, 128.15 (d, $J(^{13}C\text{-}^{31}P)$ = 23.0 Hz), 128.21 (d, $J(^{13}C\text{-}^{31}P)$ = 8.4 Hz), 126.90 (d, $J(^{13}C\text{-}^{31}P)$ = 37.6 Hz), 118.77 (d, $J(^{13}C\text{-}^{31}P)$ = 8.4 Hz), 112.85, 55.16. ^{31}P NMR (300 MHz, $CDCl_3$) δ 25.26 (s). HRMS-TOF-ES-MS Calcd for $C_{33}H_{25}AuClOP{\cdot}Na$: 723.0895 ($M^+$). Found: 723.0919. Anal. Calcd for $C_{33}H_{25}AuClOP{\cdot}H_2O$: C, 55.13; H, 3.79. Found: C, 55.21; H, 3.91.

Gold(I)-complex (49)



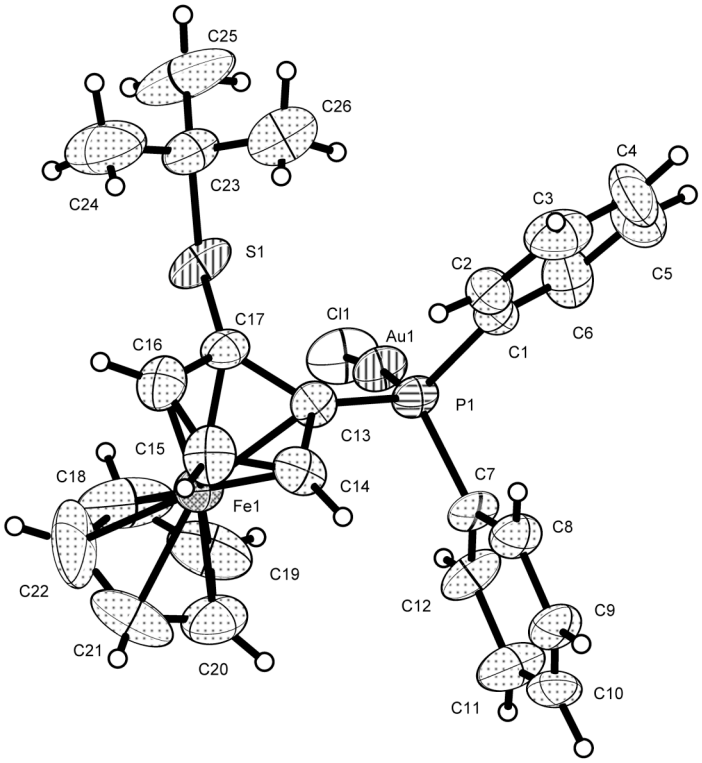
Vitreous solid; $[\alpha]^{25}$ = + 10 (c = 0.10, $CHCl_3$); ^1H NMR (300 MHz, $CDCl_3$) δ 8.00 (d, J = 8.49 Hz, 1H), 7.85 (d, J = 8.09 Hz, 1H), 7.69 (dd, J = 11.72, 1.72 Hz, 1H), 7.65 (d, J = 11.73, 2.03 Hz, 1H), 7.45 (dd, J = 8.49, 7.78 Hz, 1H), 7.37-7.16 (m, 24 H), 6.74-6.62 (m, 3H), - 0.18 (d, J = 7.9 Hz, 6H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 134.70 (d, $J(^{13}C\text{-}^{31}P)$ = 11.5 Hz), 134.57 (d, $J(^{13}C\text{-}^{31}P)$ = 10.5 Hz), 133.20, 132.58, 131.08, 130.20 (d, $J(^{13}C\text{-}^{31}P)$ = 11.5 Hz), 128.80 (d, $J(^{13}C\text{-}^{31}P)$ = 6.3 Hz), 128.54 (d, $J(^{13}C\text{-}^{31}P)$ = 4.2 Hz), 128.39 (d, $J(^{13}C\text{-}^{31}P)$ = 4.2 Hz), 127.95, 127.55, 127.35, 125.93, 8.00 (d, $J(^{13}C\text{-}^{31}P)$ = 96.23 Hz). HRMS-TOF-ES-MS Calcd for $C_{34}H_{28}Au_2P_2$: 861.1260 (M^+). Found: 861.1250.

Gold(I)-complex (50)



White solid: ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.92 (d, J = 9.1 Hz, 2H), 7.74 (d, J = 8.3 Hz, 2H), 7.68-7.59 (m, 5H), 7.50-7.35 (m, 6H), 7.25-7.22 (m, 7H), 6.86-6.79 (m, 6H), 6.65 (d, J = 7.9 Hz, 4H), 6.52 (d, J = 8.1 Hz, 1H), 2.39 (s, 6H), 2.19 (s, 6H); ^{31}P NMR (121.5 MHz, $CDCl_3$) δ 27.93 (br m).

X-ray Structure of Complex 39



Yellow crystals of **39** suitable for X-ray diffraction studies were obtained by slow diffusion of hexane vapour into a $CHCl_3$ solution at 4°C. Crystals were mounted on a glass fibre and transferred to a Bruker Smart 6K CCD area-detector-three-circle diffractometer with a MAC Science Co., LTd. Rotating Anode (CuK_α λ = 1.54178 Å) generator equipped with Goebel mirrors at settings of 50 kV and 100 mA.[3] X-ray data were collected at 296K, with a combination of seven runs at different φ and 2θ angles, 3600 frames. The data were collected using 0.3° wide ω scans (3 sec./frame at 2θ = 50° and 8 sec./frame at 2θ = 100°), crystal-to-detector distance of 4.0 cm.

The substantial redundancy in data allows empirical absorption corrections (SADABS)[4] to be applied using multiple measurements of symmetry-equivalent reflections. The raw intensity data frames were integrated with the SAINT program,[5] which also applied corrections for Lorentz and polarization effects. The software package SHELXTL version 6.10 was used for

space group determination structure solution and refinement.[6] The structure was solved by direct methods (SHEXS-97),[7] completed with difference Fourier syntheses, and refined with full-matrix-least-squares using SHELXL-97[7] minimizing $\omega(F_0^2-F_c^2)^2$. Weighted R factors (R_w) and all goodness of fit S are based on F^2; conventional R factors (R) are based on F. All non-hydrogen atoms were refined with anisotropic displacement parameters. All scattering factors and anomalous dispersions factors are contained in the SHELXTL 6.10 program library. The collection parameters, crystal and data determination data are shown in **Table 1**.

Table 1. Parameters.

Diffractometer	Bruker-Siemens Smart CCD
Radiation	CuK_α λ = 1.54178 Å
T (K)	296
θ (^{o})	4.08-66.57
Crystal degradation	inappreciable
Index Ranges	-13<=h<=13, -11<=k<=16, -20<=l<=14

Table 2. Crystal data.

Formula	$C_{26}H_{27}AuClFePS$
Molecular weight	690.77
Crystal dimensions	0.30 x 0.17 x 0.07 mm^3
Crystal system	Orthorhombic
Symmetry Group	$P2_12_12_1$
a, (Å)	11.04960(10)

b, (Å)	14.0729(3)
c, (Å)	16.9897(3)
α, (°)	90°.
β, (°)	90°
γ, (°)	90°
Volumen ($Å^3$)	2641.90(8)
Z	4
Calculated density (Mg/m^3)	1.737
F(000)	1344
μ (mm^{-1})	17.010

Table 3. Determination data and goodness of fit.

Number of reflections observed	10201
Number of independent reflections	4021
Δρ (e $Å^{-3}$) max. and min.	1.785, -4.566
R factors	R1 = 0.0555, wR2 = 0.1337
Final R [I>2σ(I)]	R1 = 0.0541, wR2 = 0.1321

Table 4. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$ x 10^3) for **39**. U(eq) is defined as one third of the trace of the orthogonalized U_{ij} tensor.

	x	y	z	U(eq)

Au(1)	9350(1)	5937(1)	6640(1)	42(1)
P(1)	7596(2)	6003(2)	7286(1)	34(1)
Cl(1)	11054(2)	5945(3)	5873(2)	64(1)
C(7)	6319(7)	5955(8)	6611(5)	36(2)
C(10)	4355(9)	5970(9)	5595(7)	53(3)
C(12)	6517(9)	6096(11)	5828(6)	53(3)
C(11)	5510(11)	6123(12)	5304(7)	66(4)
Fe(1)	7548(1)	8410(1)	7340(1)	40(1)
C(14)	6251(9)	7609(9)	7884(6)	44(3)
C(13)	7366(8)	7081(8)	7822(6)	36(2)
C(15)	6471(10)	8429(10)	8326(6)	52(3)
C(3)	6342(13)	4413(14)	9127(8)	76(5)
C(2)	6641(10)	5187(10)	8662(6)	46(3)
C(8)	5152(9)	5824(9)	6890(6)	46(3)
C(9)	4154(9)	5849(10)	6376(7)	53(3)
C(1)	7299(8)	5046(8)	7964(7)	39(3)
C(19)	8222(17)	8317(15)	6222(8)	84(6)
C(17)	8288(9)	7652(8)	8233(5)	38(2)
C(18)	8913(14)	8900(20)	6676(10)	108(9)
C(21)	7024(18)	9499(14)	6621(10)	88(6)
C(16)	7707(11)	8485(10)	8532(6)	48(3)
C(4)	6757(15)	3482(12)	8931(11)	76(4)
S(1)	9841(2)	7383(3)	8277(2)	56(1)
C(6)	7696(11)	4160(11)	7780(8)	60(3)

C(22)	8180(30)	9669(17)	6942(10)	130(11)
C(5)	7412(16)	3359(12)	8258(12)	86(5)
C(20)	7086(14)	8667(13)	6184(7)	72(5)
C(23)	10120(12)	7147(12)	9325(7)	59(3)
C(24)	10040(20)	8004(14)	9816(9)	106(7)
C(25)	11408(17)	6759(18)	9326(11)	125(10)
C(26)	9240(20)	6362(17)	9615(14)	139(10)

Table 5. Bond lengths [Å] and angles [°] for **39**.

Au(1)-P(1)	2.230(2)	Fe(1)-C(21)	2.044(14)
Au(1)-Cl(1)	2.289(2)	Fe(1)-C(19)	2.045(13)
P(1)-C(13)	1.787(12)	Fe(1)-C(13)	2.052(12)
P(1)-C(1)	1.802(11)	Fe(1)-C(15)	2.056(10)
P(1)-C(7)	1.820(8)	Fe(1)-C(20)	2.061(12)
C(7)-C(12)	1.362(14)	C(14)-C(15)	1.397(18)
C(7)-C(8)	1.387(14)	C(14)-C(13)	1.443(14)
C(10)-C(9)	1.356(17)	C(13)-C(17)	1.474(14)
C(10)-C(11)	1.385(17)	C(15)-C(16)	1.413(17)
C(12)-C(11)	1.425(14)	C(3)-C(2)	1.385(19)
Fe(1)-C(18)	2.007(15)	C(3)-C(4)	1.43(2)
Fe(1)-C(22)	2.021(17)	C(2)-C(1)	1.404(16)
Fe(1)-C(17)	2.028(9)	C(8)-C(9)	1.407(14)
Fe(1)-C(16)	2.036(10)	C(1)-C(6)	1.359(18)
Fe(1)-C(14)	2.044(11)	C(19)-C(20)	1.35(2)

C(19)-C(18)	1.36(3)	C(18)-Fe(1)-C(22)	41.3(10)
C(17)-C(16)	1.430(17)	C(18)-Fe(1)-C(17)	107.4(5)
C(17)-S(1)	1.758(10)	C(22)-Fe(1)-C(17)	124.9(9)
C(18)-C(22)	1.42(4)	C(18)-Fe(1)-C(16)	118.4(7)
C(21)-C(20)	1.39(3)	C(22)-Fe(1)-C(16)	104.9(7)
C(21)-C(22)	1.41(3)	C(17)-Fe(1)-C(16)	41.2(5)
C(4)-C(5)	1.36(2)	C(18)-Fe(1)-C(14)	166.4(9)
S(1)-C(23)	1.839(12)	C(22)-Fe(1)-C(14)	151.3(11)
C(6)-C(5)	1.42(2)	C(17)-Fe(1)-C(14)	69.8(4)
C(23)-C(24)	1.47(2)	C(16)-Fe(1)-C(14)	68.9(5)
C(23)-C(25)	1.52(2)	C(18)-Fe(1)-C(21)	67.5(7)
C(23)-C(26)	1.55(3)	C(22)-Fe(1)-C(21)	40.6(9)
P(1)-Au(1)-Cl(1)	174.25(10)	C(17)-Fe(1)-C(21)	162.9(8)
C(13)-P(1)-C(1)	106.4(5)	C(16)-Fe(1)-C(21)	125.4(7)
C(13)-P(1)-C(7)	104.0(5)	C(14)-Fe(1)-C(21)	119.0(6)
C(1)-P(1)-C(7)	103.6(5)	C(18)-Fe(1)-C(19)	39.3(8)
C(13)-P(1)-Au(1)	114.1(3)	C(22)-Fe(1)-C(19)	67.6(9)
C(1)-P(1)-Au(1)	116.3(3)	C(17)-Fe(1)-C(19)	121.0(6)
C(7)-P(1)-Au(1)	111.2(3)	C(16)-Fe(1)-C(19)	153.7(7)
C(12)-C(7)-C(8)	120.2(8)	C(14)-Fe(1)-C(19)	129.9(7)
C(12)-C(7)-P(1)	119.1(6)	C(21)-Fe(1)-C(19)	66.1(7)
C(8)-C(7)-P(1)	120.6(7)	C(18)-Fe(1)-C(13)	127.8(8)
C(9)-C(10)-C(11)	121.3(9)	C(22)-Fe(1)-C(13)	165.1(11)
C(7)-C(12)-C(11)	119.2(9)	C(17)-Fe(1)-C(13)	42.4(4)
C(10)-C(11)-C(12)	119.5(10)	C(16)-Fe(1)-C(13)	70.1(5)

C(14)-Fe(1)-C(13)	41.3(4)	C(17)-C(13)-P(1)	127.3(7)
C(21)-Fe(1)-C(13)	153.5(7)	C(14)-C(13)-Fe(1)	69.1(6)
C(19)-Fe(1)-C(13)	110.4(6)	C(17)-C(13)-Fe(1)	68.0(6)
C(18)-Fe(1)-C(15)	152.7(8)	P(1)-C(13)-Fe(1)	123.8(5)
C(22)-Fe(1)-C(15)	117.5(9)	C(14)-C(15)-C(16)	110.4(11)
C(17)-Fe(1)-C(15)	68.3(4)	C(14)-C(15)-Fe(1)	69.6(6)
C(16)-Fe(1)-C(15)	40.4(5)	C(16)-C(15)-Fe(1)	69.1(6)
C(14)-Fe(1)-C(15)	39.9(5)	C(2)-C(3)-C(4)	120.8(14)
C(21)-Fe(1)-C(15)	108.3(6)	C(3)-C(2)-C(1)	119.6(14)
C(19)-Fe(1)-C(15)	165.7(7)	C(7)-C(8)-C(9)	120.8(10)
C(13)-Fe(1)-C(15)	68.3(5)	C(10)-C(9)-C(8)	118.8(10)
C(18)-Fe(1)-C(20)	65.8(6)	C(6)-C(1)-C(2)	119.4(11)
C(22)-Fe(1)-C(20)	67.2(7)	C(6)-C(1)-P(1)	118.6(9)
C(17)-Fe(1)-C(20)	154.9(6)	C(2)-C(1)-P(1)	121.9(9)
C(16)-Fe(1)-C(20)	163.8(7)	C(20)-C(19)-C(18)	109.1(18)
C(14)-Fe(1)-C(20)	110.8(5)	C(20)-C(19)-Fe(1)	71.5(8)
C(21)-Fe(1)-C(20)	39.5(7)	C(18)-C(19)-Fe(1)	68.9(9)
C(19)-Fe(1)-C(20)	38.4(7)	C(16)-C(17)-C(13)	107.8(9)
C(13)-Fe(1)-C(20)	121.1(6)	C(16)-C(17)-S(1)	126.8(8)
C(15)-Fe(1)-C(20)	129.1(6)	C(13)-C(17)-S(1)	125.2(8)
C(15)-C(14)-C(13)	108.5(10)	C(16)-C(17)-Fe(1)	69.7(6)
C(15)-C(14)-Fe(1)	70.5(7)	C(13)-C(17)-Fe(1)	69.7(5)
C(13)-C(14)-Fe(1)	69.7(6)	S(1)-C(17)-Fe(1)	122.6(5)
C(14)-C(13)-C(17)	105.9(10)	C(19)-C(18)-C(22)	108.7(17)
C(14)-C(13)-P(1)	126.6(8)	C(19)-C(18)-Fe(1)	71.8(9)

C(22)-C(18)-Fe(1)	69.9(10)
C(20)-C(21)-C(22)	107.8(18)
C(20)-C(21)-Fe(1)	70.9(9)
C(22)-C(21)-Fe(1)	68.8(10)
C(15)-C(16)-C(17)	107.4(10)
C(15)-C(16)-Fe(1)	70.5(6)
C(17)-C(16)-Fe(1)	69.1(5)
C(5)-C(4)-C(3)	118.8(14)
C(17)-S(1)-C(23)	104.1(5)
C(1)-C(6)-C(5)	121.5(13)
C(21)-C(22)-C(18)	105.4(17)
C(21)-C(22)-Fe(1)	70.6(10)
C(18)-C(22)-Fe(1)	68.8(11)
C(4)-C(5)-C(6)	119.7(16)
C(19)-C(20)-C(21)	109.2(16)
C(19)-C(20)-Fe(1)	70.2(8)
C(21)-C(20)-Fe(1)	69.6(8)
C(24)-C(23)-C(25)	110.7(13)
C(24)-C(23)-C(26)	111.5(17)
C(25)-C(23)-C(26)	109.1(17)
C(24)-C(23)-S(1)	113.0(11)
C(25)-C(23)-S(1)	102.8(11)
C(26)-C(23)-S(1)	109.4(10)

Table 6. Anisotropic displacement parameters ($Å^2$ x 10^3) for **39**. The anisotropic displacement factor exponent takes the form: $-2\pi^2[(ha^*)^2U_{11}+ ... + 2hka+b+U_{12}]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
Au(1)	18(1)	59(1)	48(1)	0(1)	1(1)	3(1)
P(1)	21(1)	45(2)	37(1)	2(1)	1(1)	-2(1)
Cl(1)	23(1)	104(3)	66(1)	6(2)	13(1)	8(1)
C(7)	6(3)	54(7)	49(5)	3(6)	-4(3)	2(3)
C(10)	35(5)	56(8)	68(6)	18(6)	-20(5)	4(6)
C(12)	26(4)	85(11)	46(5)	-13(6)	-6(4)	-3(5)
C(11)	47(6)	106(13)	46(5)	10(7)	-10(5)	-10(7)
Fe(1)	33(1)	48(1)	40(1)	7(1)	2(1)	-4(1)
C(14)	31(5)	51(8)	50(5)	15(5)	10(4)	0(5)
C(13)	20(4)	41(7)	47(5)	2(5)	5(3)	1(4)
C(15)	56(6)	55(8)	45(5)	-9(6)	16(5)	-1(5)
C(3)	67(8)	108(16)	53(6)	32(8)	-12(6)	-23(8)
C(2)	50(6)	45(8)	45(5)	8(5)	-5(4)	-8(5)
C(8)	29(5)	58(9)	53(5)	9(6)	-5(4)	-3(5)
C(9)	26(5)	65(9)	67(6)	14(6)	-13(4)	-12(5)
C(1)	19(4)	40(7)	59(5)	13(5)	-7(4)	-3(4)
C(19)	88(12)	109(15)	56(7)	33(9)	30(8)	31(11)
C(17)	39(5)	49(7)	25(4)	7(4)	-2(3)	-5(4)
C(18)	44(8)	200(30)	77(10)	69(16)	0(7)	-9(11)
C(21)	102(13)	86(14)	76(9)	49(11)	27(10)	36(10)
C(16)	56(6)	54(9)	35(5)	-6(5)	6(4)	-7(5)

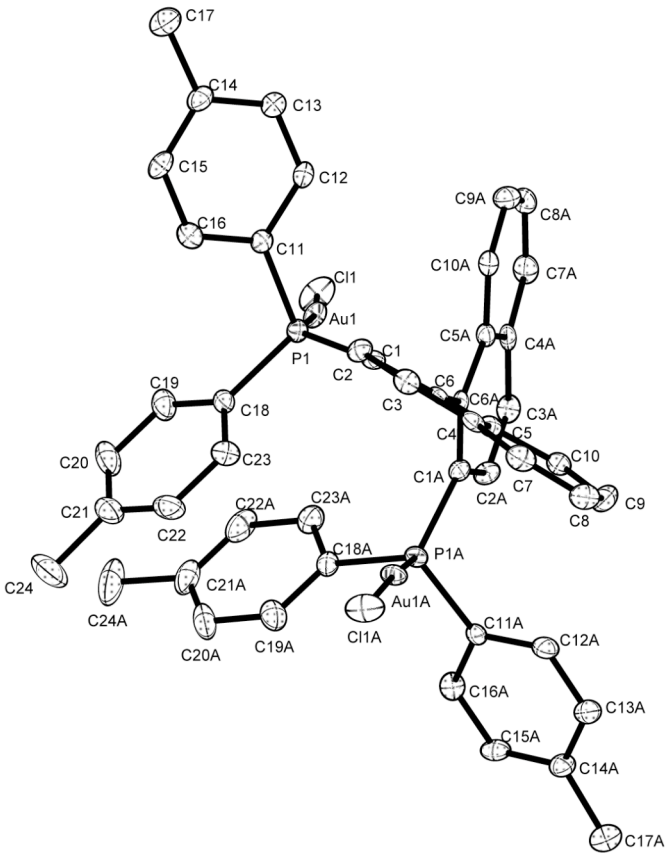
C(4)	79(10)	39(10)	110(12)	26(9)	-3(9)	-12(7)
S(1)	31(1)	89(3)	47(1)	-10(2)	-8(1)	-3(1)
C(6)	56(7)	49(10)	77(7)	-2(7)	5(6)	-1(6)
C(22)	240(30)	79(16)	69(10)	28(11)	-6(16)	-101(19)
C(5)	81(10)	50(11)	128(15)	11(11)	-27(11)	7(8)
C(20)	73(9)	96(14)	47(6)	22(8)	-13(6)	-14(8)
C(23)	61(7)	66(10)	51(6)	-3(7)	-22(5)	0(7)
C(24)	130(16)	117(18)	71(9)	-26(10)	-45(10)	40(13)
C(25)	84(11)	190(30)	97(11)	-60(14)	-53(10)	71(14)
C(26)	170(30)	113(19)	138(18)	11(16)	-96(19)	-22(17)

Table 7. Hydrogen coordinates (x 10^4) and isotropic displacement parameters (Å^2 x 10^3) for **39**.

	x	y	z	U(eq)
H(10)	3705	5951	5248	63
H(12)	7300	6173	5638	63
H(11)	5628	6242	4771	80
H(14)	5512	7434	7667	53
H(15)	5886	8873	8465	62
H(3)	5866	4502	9572	91
H(2)	6408	5796	8810	56
H(8)	5027	5718	7424	56
H(9)	3371	5783	6568	63

H(19)	8490	7765	5977	101
H(18)	9728	8818	6793	129
H(21)	6342	9878	6690	106
H(16)	8076	8975	8811	58
H(4)	6583	2968	9256	91
H(6)	8165	4074	7331	73
H(22)	8414	10174	7261	156
H(5)	7671	2756	8113	104
H(20)	6446	8394	5909	86
H(24A)	9201	8170	9889	159
H(24B)	10449	8519	9560	159
H(24C)	10403	7885	10318	159
H(25A)	11952	7237	9133	187
H(25B)	11449	6209	8992	187
H(25C)	11633	6586	9852	187
H(26A)	9539	6102	10101	209
H(26B)	9196	5867	9227	209
H(26C)	8455	6629	9697	209

X-ray Structure of Complex 47



Colorless crystals of **47** suitable for X-ray diffraction studies were obttained by slow diffusion of hexane vapour into a $CHCl_3$ solution at 4 ^oC. Crystals were mounted on a glass fiber and transferred to a Bruker Smart 6K CCD area-detector-three-circle diffractometer with a MAC Science Co., LTd. Rotating Anode (CuK_α λ = 1.54178 Å) generator equipped with Goebel mirrors at settings of 50 kV and 100 mA. X-ray data were collected at 100K, with a combination of seven runs at different φ and 2θ angles, 3600 frames. The data were collected using 0.3^o wide ω scans (3 sec./frame at 2θ = 50^o and 5 sec./frame at 2θ = 100^o), crystal-to-detector distance of 4.0 cm. The collection parameters, crystal and data determination data are shown in **Tables 8-14**.

Table 8. Parameters.

Diffractometer	Bruker-Siemens Smart CCD

Radiation	CuK_α λ = 1.54178 Å
T (K)	293
θ (^{o})	4.49-70.49
Crystal degradation	inappreciable
Index Ranges	-13<=h<=12, -12<=k<=13, -27<=l<=32

Table 9. Crystal data.

Formula	C48 H40 Au2 Cl2 P2
Molecular weight	1143.57
Crystal dimensions	0.20 x 0.09 x 0.04 mm^3
Crystal system	Trigonal
Symmetry Group	$P3_221$
a, (Å)	11.37890(10)
b, (Å)	11.37890(10)
c, (Å)	27.7151(3)
α, (^{o})	90°.
β, (^{o})	90°
γ, (^{o})	120°
Volumen ($Å^3$)	3107.76(5)
Z	3

Calculated density (Mg/m^3)	1.833
F(000)	1650
μ (mm^{-1})	15.289

Table 10. Determination data and goodness of fit.

Number of reflections observed	12054
Number of independent reflections	3778
$\Delta\rho$ (e $Å^{-3}$) max. and min.	0.461, -0.513
R factors	R1 = 0.0185, wR2 = 0.0450
Final R [$I>2\sigma(I)$]	R1 = 0.0183, wR2 = 0.0448

Table 11. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$ x 10^3) for **47**. U(eq) is defined as one third of the trace of the orthogonalized U_{ij} tensor.

	x	y	z	U(eq)
Au(1)	7025(1)	9022(1)	3126(1)	14(1)
Cl(1)	5725(1)	8136(1)	2449(1)	27(1)
P(1)	8146(1)	9623(1)	3827(1)	11(1)
C(1)	9498(4)	11345(4)	3950(1)	13(1)
C(2)	9904(4)	11669(4)	4441(1)	14(1)
C(3)	11048(4)	12843(4)	4564(1)	15(1)
C(4)	11837(4)	13813(3)	4206(1)	14(1)

C(5)	11383(4)	13543(4)	3717(1)	12(1)
C(6)	10216(4)	12288(3)	3593(1)	10(1)
C(7)	13065(4)	15003(4)	4317(1)	19(1)
C(8)	13815(4)	15924(4)	3968(1)	21(1)
C(9)	13344(4)	15711(4)	3487(1)	20(1)
C(10)	12156(4)	14553(4)	3366(1)	17(1)
C(11)	6891(3)	9212(3)	4299(1)	12(1)
C(12)	6021(4)	9745(4)	4278(1)	18(1)
C(13)	4948(4)	9318(4)	4594(1)	21(1)
C(14)	4697(4)	8328(4)	4947(1)	18(1)
C(15)	5595(4)	7846(4)	4978(1)	17(1)
C(16)	6672(4)	8262(4)	4659(1)	15(1)
C(17)	3467(4)	7786(5)	5269(2)	28(1)
C(18)	8935(4)	8597(4)	3936(1)	15(1)
C(19)	8254(4)	7256(4)	3776(1)	23(1)
C(20)	8821(5)	6448(4)	3835(1)	29(1)
C(21)	10074(5)	6934(5)	4054(2)	30(1)
C(22)	10755(5)	8269(5)	4211(2)	29(1)
C(23)	10189(4)	9091(4)	4154(1)	22(1)
C(24)	10722(7)	6067(6)	4109(2)	48(2)

Table 12. Bond lengths [Å] and angles [°] for **47**.

Au(1)-P(1)	2.2353(8)	P(1)-C(18)	1.819(4)
Au(1)-Cl(1)	2.2880(9)	P(1)-C(1)	1.819(4)
P(1)-C(11)	1.818(3)	C(1)-C(6)	1.386(5)

C(1)-C(2)	1.426(5)	C(11)-P(1)-C(18)	106.99(16)
C(2)-C(3)	1.362(5)	C(11)-P(1)-C(1)	105.92(16)
C(3)-C(4)	1.421(5)	C(18)-P(1)-C(1)	103.71(18)
C(4)-C(7)	1.410(5)	C(11)-P(1)-Au(1)	107.04(11)
C(4)-C(5)	1.427(5)	C(18)-P(1)-Au(1)	109.73(12)
C(5)-C(6)	1.423(5)	C(1)-P(1)-Au(1)	122.55(12)
C(5)-C(10)	1.424(5)	C(6)-C(1)-C(2)	119.5(3)
C(6)-C(6)#1	1.500(7)	C(6)-C(1)-P(1)	123.6(3)
C(7)-C(8)	1.367(6)	C(2)-C(1)-P(1)	116.6(3)
C(8)-C(9)	1.413(5)	C(3)-C(2)-C(1)	121.3(3)
C(9)-C(10)	1.376(6)	C(2)-C(3)-C(4)	120.7(3)
C(11)-C(12)	1.397(5)	C(7)-C(4)-C(3)	122.1(3)
C(11)-C(16)	1.400(5)	C(7)-C(4)-C(5)	119.5(3)
C(12)-C(13)	1.380(5)	C(3)-C(4)-C(5)	118.4(3)
C(13)-C(14)	1.408(5)	C(6)-C(5)-C(10)	122.3(3)
C(14)-C(15)	1.382(6)	C(6)-C(5)-C(4)	120.1(3)
C(14)-C(17)	1.508(5)	C(10)-C(5)-C(4)	117.6(3)
C(15)-C(16)	1.388(5)	C(1)-C(6)-C(5)	119.8(3)
C(18)-C(23)	1.384(6)	C(1)-C(6)-C(6)#1	122.7(4)
C(18)-C(19)	1.393(6)	C(5)-C(6)-C(6)#1	117.4(3)
C(19)-C(20)	1.372(6)	C(8)-C(7)-C(4)	121.3(3)
C(20)-C(21)	1.384(7)	C(7)-C(8)-C(9)	120.0(4)
C(21)-C(22)	1.386(7)	C(10)-C(9)-C(8)	120.0(4)
C(21)-C(24)	1.506(6)	C(9)-C(10)-C(5)	121.5(4)
C(22)-C(23)	1.385(6)	C(12)-C(11)-C(16)	118.4(3)
P(1)-Au(1)-Cl(1)	172.69(4)	C(12)-C(11)-P(1)	119.6(3)

C(16)-C(11)-P(1)	121.7(3)
C(13)-C(12)-C(11)	120.9(3)
C(12)-C(13)-C(14)	120.9(4)
C(15)-C(14)-C(13)	117.8(3)
C(15)-C(14)-C(17)	121.3(3)
C(13)-C(14)-C(17)	120.9(4)
C(14)-C(15)-C(16)	121.7(3)
C(15)-C(16)-C(11)	120.2(3)
C(23)-C(18)-C(19)	118.6(4)
C(23)-C(18)-P(1)	123.5(3)
C(19)-C(18)-P(1)	117.8(3)
C(20)-C(19)-C(18)	120.4(4)
C(19)-C(20)-C(21)	121.3(4)
C(20)-C(21)-C(22)	118.3(4)
C(20)-C(21)-C(24)	121.8(5)
C(22)-C(21)-C(24)	119.8(5)
C(23)-C(22)-C(21)	120.7(4)
C(18)-C(23)-C(22)	120.6(4)

Table 13. Anisotropic displacement parameters ($Å^2$ x 10^3) for **47**. The anisotropic displacement factor exponent takes the form: $-2\pi^2[(ha^*)^2U_{11}+ ... + 2hka+b+U_{12}]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
Au(1)	13(1)	12(1)	11(1)	-1(1)	-1(1)	3(1)
Cl(1)	23(1)	30(1)	14(1)	-5(1)	-5(1)	3(1)
P(1)	11(1)	11(1)	11(1)	0(1)	-1(1)	5(1)
C(1)	9(2)	13(2)	18(2)	-1(1)	0(1)	6(2)
C(2)	14(2)	18(2)	11(2)	2(1)	1(1)	8(2)
C(3)	18(2)	20(2)	10(2)	-2(1)	-3(1)	12(2)
C(4)	14(2)	13(2)	18(2)	-4(1)	-2(1)	10(2)
C(5)	12(2)	11(2)	14(2)	-4(1)	-1(1)	6(1)
C(6)	13(2)	12(2)	11(2)	1(1)	1(1)	10(2)
C(7)	16(2)	19(2)	22(2)	-7(2)	-6(2)	9(2)
C(8)	13(2)	14(2)	29(2)	-11(2)	-4(2)	4(2)
C(9)	19(2)	17(2)	21(2)	2(2)	6(2)	6(2)
C(10)	18(2)	15(2)	19(2)	-1(1)	4(2)	10(2)
C(11)	12(2)	9(2)	11(2)	-4(1)	-1(1)	3(1)
C(12)	17(2)	14(2)	22(2)	6(1)	3(2)	7(2)
C(13)	17(2)	18(2)	27(2)	4(2)	4(2)	9(2)
C(14)	18(2)	17(2)	16(2)	0(1)	5(2)	7(2)
C(15)	16(2)	17(2)	12(2)	3(2)	2(1)	4(2)
C(16)	17(2)	19(2)	13(2)	-2(1)	-5(2)	10(2)
C(17)	25(2)	28(2)	30(2)	4(2)	9(2)	11(2)
C(18)	20(2)	17(2)	13(2)	5(1)	5(1)	12(2)

C(19)	34(3)	21(2)	18(2)	4(2)	5(2)	17(2)
C(20)	50(3)	25(2)	23(2)	3(2)	9(2)	26(2)
C(21)	41(3)	39(3)	24(2)	14(2)	16(2)	32(2)
C(22)	26(2)	42(3)	30(2)	13(2)	7(2)	25(2)
C(23)	20(2)	24(2)	26(2)	2(2)	3(2)	13(2)
C(24)	71(4)	61(4)	46(3)	17(3)	22(3)	58(3)

Table 14. Hydrogen coordinates (x 10^4) and isotropic displacement parameters (Å^2 x 10^3) for **47**.

	x	y	z	U(eq)
H(2)	9378	11066	4682	17
H(3)	11315	13011	4885	18
H(7)	13370	15164	4635	23
H(8)	14634	16690	4047	25
H(9)	13837	16353	3251	24
H(10)	11851	14427	3049	20
H(12)	6168	10398	4047	22
H(13)	4384	9689	4575	25
H(15)	5474	7227	5219	20
H(16)	7249	7907	4685	18
H(17A)	2704	7052	5109	43
H(17B)	3270	8496	5338	43
H(17C)	3644	7464	5565	43
H(19)	7410	6907	3629	28

H(20)	8355	5557	3725	35
H(22)	11602	8617	4355	35
H(23)	10655	9983	4264	27
H(24A)	11668	6592	4030	72
H(24B)	10287	5300	3897	72
H(24C)	10624	5756	4437	72

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