Bis-phosphine allene ligands: coordination chemistry and preliminary applications in catalysis

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Table of contents

1. General information
2. Experimental details and analytical data
3. Spectral data
4. X-Ray crystal structure determination
5. Chiral HPLC analyses
6. MS of bridge gold complex
7. References
1. General information

All reactions were performed in oven-dried glassware under argon atmosphere. All solvents were freshly distilled prior to use: Et₂O and THF over sodium and benzophenone; CH₂Cl₂ over CaH₂. DMF was dried and degassed before using. n-Butyllithium was purchased as 2.5 M solutions in hexanes and titrated before using. NaH was purchased as a 60% suspension in mineral oil and washed with pentane under argon atmosphere before using. Column chromatography was performed on Merck Geduran SI 60 A silica gel (35-70 mm). Analytical Thin-layer chromatography (TLC) was performed on Merck 60 F₂₅₄ silica gel and visualized either with a UV lamp (254 nm), or using solutions of p-anisaldehyde-sulfuric acid-acetic acid in EtOH or KMnO₄-K₂CO₃ in water followed by heating. ¹H NMR spectra were recorded at 400 MHz, 300 MHz or 600 MHz and data are reported as follows: chemical shift in ppm with the solvent as an internal indicator (CDCl₃ δ 7.26, CD₂Cl₂ δ 5.32, C₆D₆ δ 7.16), multiplicity (s = singlet, d = doublet, t = triplet, q = quartet or m = multiple and b = broad) and integration. ¹³C NMR spectra were recorded at 100 MHz, 75 MHz or 151 MHz and data are reported as follows: chemical shift in ppm with the solvent as an internal indicator (CDCl₃ δ 77.16, CD₂Cl₂ δ 54.00, C₆D₆ δ 128.06). ³¹P NMR spectra were recorded at 122 MHz or 162 MHz and data are reported as follows: chemical shift in ppm with an internal probe of H₃PO₄ (85% in H₂O, δ 0.0). Coupling constants (J) are given in Hertz (Hz). High-resolution mass spectra (HRMS) were obtained using a mass spectrometer MicroTOF from Bruker with an electron spray ion source (ESI) and a TOF detector at Institut Parisien de Chimie Moléculaire. Melting points (m.p.) were recorded with a SMP3 Stuart Scientific melting point apparatus. Infrared (IR) spectra were measured using Tensor 27 (ATR Diamond) Bruker spectrometer. IR data are reported as characteristic band (cm⁻¹) in their maximal intensity. Optical rotations were determined using a JASCO P2000. Chiral HPLC analyses were achieved on an Agilent 1260 infinity unit with pump, autosampler, oven, DAD and Jasco CD-2095 circular dichroism detector, controlled by a SRA Instrument software (Marcy l'Etoile, France) at Institut des Sciences Moléculaires de Marseille.
2. Experimental details and analytical data

1,3-Bis(diphenylphosphino)-1,3-diphenylpropa-1,2-diene (1)

To a solution of 1,3-diphenyl-1-propyne \(^1\) (1.50 g, 7.80 mmol, 1 equiv) in THF (80 mL) was added \(n\)-BuLi (6.24 mL of 2.5 M in hexane, 15.60 mmol, 2 equiv) at \(-78\) °C. The solution of chlorodiphenylphosphine (2.9 mL, 15.60 mmol, 2 equiv) in THF (10 mL) was slowly added into the mixture at the same temperature. The mixture was slowly warmed to room temperature for 15 h and concentrated under reduce pressure. The residue was precipitated in the mixture of ethanol and water (1:1) to obtain 1 (2.12 g, 48% yield) as a white solid. (Note: The product was stable in the solid under argon atmosphere and slowly oxidized in small amount of oxygen). The characterization data were identical to those previously reported.\(^2\)

m.p. = 160–163 °C.

IR (neat): \(\tilde{\nu} \text{ (cm}^{-1}\text{)} = 3057, 2226, 1902, 1595, 1492, 1437, 1187, 1120, 729, 694.\)

\(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta 7.47\) (d, \(J = 8.4\) Hz, 5H), 7.35-7.12 (m, 22H), 7.01 (t, \(J = 7.7\) Hz, 3H).

\(^{13}\)C NMR (100 MHz, CDCl\(_3\)) \(\delta 209.9\) (d, \(2J_{CP} = 3.5\) Hz, C), 136.0, 135.9, 135.8, 135.6, 135.2, 135.0, 134.9, 134.8, 133.8 (2CH), 133.6, 132.0, 131.7, 131.6, 129.6, 129.2 (2CH), 128.8, 128.7, 128.6, 128.5, 128.4, 128.3 (2CH), 128.2 (2CH), 128.1 (2CH), 128.0, 127.7, 127.4, 127.2, 127.1, 127.0 (CH), 105.0 (d, \(^1J_{CP} = 3.6\) Hz, C), 104.8 (d, \(^1J_{CP} = 3.0\) Hz, C).

\(^{31}\)P NMR (162 MHz, CDCl\(_3\)) \(\delta -8.8.\)

HRMS (ESI) calced. for C\(_{39}\)H\(_{30}\)P\(_2\)H ([M + H]\(^+\)) 561.18955 found 561.18941.

1,3-Bis(diphenylphosphoroselenoyl)-1,3-diphenylpropa-1,2-diene (2)

The solution of 1 (0.10 g, 0.18 mmol, 1 equiv) and small pieces of selenium (0.08 g, 1.03 mmol, 7.2 equiv) in CDCl\(_3\) (17 mL) was stirred at reflux overnight (24 h). After monitoring the reaction by \(^{31}\)P NMR, the mixture was filtered to remove selenium and concentrated to afford 2 (0.17 g, quant) as a yellow solid.

The characterization data were identical to those previously reported.\(^2\)

m.p. = 207–208 °C.

IR (neat): \(\tilde{\nu} \text{ (cm}^{-1}\text{)} = 3079, 2221, 1899, 1594, 1492, 1435, 1335, 1184, 1095, 1029, 999, 908, 715.\)

\(^1\)H NMR (300 MHz, CDCl\(_3\)) \(\delta 7.63-7.46\) (m, 10H), 7.41-7.19 (m, 20H).

\(^{13}\)C NMR (100 MHz, CDCl\(_3\)) \(\delta 211.8\) (t, \(2J_{CP} = 5.0\) Hz), 133.2, 133.1, 132.7, 132.6, 132.0, 131.4, 130.8, 130.7, 129.7, 128.7, 128.5, 105.4 (d, \(^1J_{CP} = 8.1\) Hz), 105.0 (d, \(^1J_{CP} = 8.3\) Hz).
\[^{31}\text{P NMR}\] (162 MHz, CDCl\textsubscript{3}) \(\delta\) 35.5 (d, \(^4J_{PP} = 15.7\) Hz), 33.2 (P=Se, \(^1J_{PSe} = 751\) Hz), 30.86 (d, \(^4J_{PP} = 16.0\) Hz).

\(\text{(Se = } ^{77}\text{Se isotope)}\)

Dichloropalladium(II)-(1,3-Diphenylpropa-1,2-diene-1,3-diyl)-bis(diphenylphosphine) (3)

A solution of 1 (0.07 g, 0.12 mmol, 1 equiv) and cis-bis(acetonitrile)dichloropalladium(II) (32 mg, 0.12 mmol, 1 equiv) in toluene (1.4 mL) was stirred at 80 °C for 4 h. The mixture was concentrated under reduced pressure. The orange solid was washed with Et\textsubscript{2}O and dried under vacuum to give 3 (74 mg, 84% yield) as a yellow solid. The latter was dissolved in dichloromethane (1 mL) and cyclohexane was added slowly in order to obtain a biphasic solution. Overnight crystallization occurred to give crystals of expected complex.

\(\text{m.p. = 236-237 °C}\)

\(\text{IR (neat): } \tilde{\nu} (\text{cm}^{-1}) = 3055, 1734, 1597, 1493, 1481, 1310, 1098, 729, 690.\)

\(^1\text{H NMR}\) (400 MHz, CD\textsubscript{2}Cl\textsubscript{2}) \(\delta\) 8.62 (b dd, \(J = 12.0, 7.2\) Hz, 4H), 7.80-7.72 (m, 6H), 7.35-7.33 (m, 2H), 7.24-7.19 (m, 8H), 7.05 (t, \(J = 7.6\) Hz, 2H), 6.86 (t, \(J = 7.6\) Hz, 4H), 6.10 (d, \(J = 7.6\) Hz, 4H).

\(^{13}\text{C NMR}\) (100 MHz, CD\textsubscript{2}Cl\textsubscript{2}) \(\delta\) 193.3 (t, \(^2J_{CP} = 3.8\) Hz), 136.9, 136.8, 136.7, 134.0, 133.9, 133.5, 133.3, 133.3, 133.1, 131.9 (2CH), 130.1 (2CH), 130.0, 129.9, 129.8, 129.5, 129.1, 129.0, 128.8, 128.7, 128.5, 128.4, 128.4, 128.3, 105.6 (t, \(^1J_{CP} = 21.7\) Hz).

\(^{31}\text{P NMR\) (162 MHz, CDCl\textsubscript{3}) \(\delta\) 128.3.\)

Dichloroplatinum(II)-(1,3-Diphenylpropa-1,2-diene-1,3-diyl)-bis(diphenylphosphine) (4)

A solution of 1 (0.15 g, 0.27 mmol, 1 equiv) and cis-bis(benzonitrile)dichloroplatinum(II) (0.12 g, 0.27 mmol, 1 equiv) in toluene (6 mL) was stirred at 80 °C for 20 h. The mixture was filtered over a short pad of Celite\textsuperscript{®} and concentrated under reduced pressure. The product was recrystallized by diffusion of toluene into the solution of the crude product in CHCl\textsubscript{3} to give 4 (0.24 g, quant) as a brown solid. \(\text{(Note: the product is not air stable).}\)

\(\text{IR (neat): } \tilde{\nu} (\text{cm}^{-1}) = 3080, 3058, 2228, 1903, 1714, 1593, 1482, 1436, 1215, 1099, 758, 716.\)

\(^1\text{H NMR\) (300 MHz, CDCl\textsubscript{3}) \(\delta\) 10.54-10.47 (m, 3H), 9.73-9.66 (m, 6H), 9.28-9.13 (m, 11H), 8.98 (t, \(J = 7.5\) Hz, 3H), 8.79 (t, \(J = 7.7\) Hz, 4H), 8.07 (d, \(J = 7.6\) Hz, 3H).

\(^{13}\text{C NMR\) (100 MHz, CDCl\textsubscript{3}) \(\delta\) 198.9 (t, \(^2J_{CP} = 5.1\) Hz, C), 136.6 (2CH), 136.5, 134.2 (2CH), 134.1, 133.2 (2CH), 131.8 (2CH), 131.7, 131.1, 130.0 (2CH), 129.9 (2CH), 129.8 (4CH), 129.7, 129.2, 128.9 (4CH), 128.7 (6CH), 128.5, 128.4, 128.3, 128.2, 128.0, 104.5 (dd, \(^1J_{CP} = 32.8, 21.5\) Hz, 2C).

\(^{31}\text{P NMR\) (162 MHz, CDCl\textsubscript{3}) \(\delta\) 98.7 (P-Pt, \(^1J_{PP,Pt} = 4371\) Hz).\)
Synthesis of polymer 6

To a solution of 1 (0.1 g, 0.18 mmol, 1 equiv) in CH₂Cl₂ (4 mL) at –20 °C was added AuCl(Me₂S) (0.051 g, 0.18 mmol, 1 equiv) in solution in CH₂Cl₂ (1 mL). The temperature was slowly warmed to room temperature and the mixture was stirred for 4 h. The mixture was concentrated under reduced pressure. The residue was dissolved in CH₂Cl₂ and precipitated with pentane to obtain 6 as a white solid. The latter was recrystallized by diffusion of pentane into the solution of crude product in CH₂Cl₂ to give 6 as a colorless crystals (0.1 g, quant).

**¹H NMR** (400 MHz, CD₂Cl₂) δ 7.50-7.38 (m, 10H, Hᵃʳ), 7.32-7.11 (m, 20H, Hᵃʳ).

**³¹P NMR** (162 MHz, CD₂Cl₂) δ 12.3 (bs), 27.9 (s).

Dichlorogold(I)-(1,3-Diphenylpropa-1,2-diene-1,3-diyl)-bis(diphenylphosphine) (rac-7)

![Dichlorogold(I)-(1,3-Diphenylpropa-1,2-diene-1,3-diyl)-bis(diphenylphosphine) (rac-7)]

A solution of AuCl(Me₂S) (0.106 g, 0.36 mmol, 2 equiv) and 1 (0.1 g, 0.18 mmol, 1 equiv) in CH₂Cl₂ (5 mL) was stirred at room temperature for 3 h. The mixture was concentrated under reduced pressure. The residue was dissolved in CH₂Cl₂ and precipitated with pentane to obtain rac-7 (0.184 g, quant) as a white solid. The latter was recrystallized by diffusion of cyclohexane into the solution of crude product in CH₂Cl₂ to give colorless crystals quantitatively.

m.p. = 259–261 °C

**IR (neat):** ʋ (cm⁻¹) = 3055, 2924, 2237, 1908, 1490, 1436, 1101, 911, 730, 689.

**¹H NMR** (400 MHz, CDCl₃) δ 7.60-7.31 (m, 30H, Hᵃʳ).

**¹³C NMR** (100 MHz, CDCl₃) δ 213.1 (t, JCP = 3.5 Hz), 135.2, 135.1, 135.0, 134.1, 134.0, 133.5, 132.9, 132.7, 132.4, 131.8, 131.5, 130.3, 130.2, 130.1, 129.8, 129.7, 129.6, 129.5, 129.4, 129.3, 129.2, 129.1 (CH₃), 129.0, 128.9, 127.8, 127.7, 127.5, 127.2, 126.8, 126.6, 104.4 (d, JCP = 8.1 Hz), 103.9 (d, JCP = 8.1 Hz).

**³¹P NMR** (162 MHz, CDCl₃) δ 30.2.

**HRMS (ESI)** calcd for C₃₉H₃₀Au₂Cl₅P₂ ([M + Na⁺]⁺) 1047.04230, found 1047.04241

**GP: Gold(I)-catalyzed cycloisomerization of enynes**

To a solution of rac-7 (0.03 equiv) in dry and degassed solvent was added AgX (X=SbF₆, OTf, BF₄ or OTs) (0.06 equiv). After 10 min stirring at room temperature, the precipitation of AgCl occurred (white solid). Then, a solution of 1,6-enyne (1 equiv) in dry and degassed solvent was added (final concentration 0.05 M). The mixture was stirred and monitored by TLC. When the reaction was complete, the mixture was filtered over a short pad of Celite® and washed with CH₂Cl₂. The solution was concentrated under reduced pressure. Subsequent purification by flash-chromatography on silica gel afforded the desired products.
3-(Propan-2-ylidene)-1-tosyl-1,2,3,6-tetrahydropyridine (9a)

According to the general procedure GP: using rac-7 (11 mg, 0.0108 mmol), AgSbF$_6$ (7.4 mg, 0.022 mmol) and 8a (100 mg, 0.36 mmol). The reaction mixture in CH$_2$Cl$_2$ (7 mL) was stirred at room temperature for 2h. Silica gel chromatography (Rf = 0.11, cyclohexane/AcOEt, 10/1) gave 9a as a white solid (77 mg, 77%). The characterization data were identical to those previously reported.\(^3\)

R$_f$ = 0.11 (EtOAc/Cyclohexane: 1/10).

**IR (neat):** $\tilde{\nu}$ (cm$^{-1}$) = 2956, 2854, 1597, 1494, 1381, 1346, 1164, 1091, 1035, 955, 910, 816, 734, 664.

$^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.64 (d, J = 8.2, 2H), 7.26 (d, J = 7.9 Hz, 2H), 6.32 (dt, J = 10.4, 2.1 Hz, 1H), 5.51 (dt, J = 10.4, 3.6 Hz, 1H), 3.89 (s, 2H), 3.75 (bs, 2H), 2.39 (s, 3H, H$_1$), 1.75 (s, 3H), 1.66 (s, 3H).

$^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 143.4, 134.3, 129.9, 129.4, 127.7, 124.6, 25.2, 21.6, 20.4, 19.7.

6-Methyl-1-phenyl-3-tosyl-3-azabicyclo[4.1.0]hept-4-ene (8b)

According to the general procedure GP: using rac-7 (11 mg, 0.0108 mmol), AgSbF$_6$ (7.4 mg, 0.022 mmol) and 8b (122 mg, 0.36 mmol). The reaction mixture in CH$_2$Cl$_2$ (7 mL) was stirred at room temperature for 2h. Silica gel chromatography (Rf = 0.3, pentane/AcOEt, 10/1) gave 9b as a white solid (103.7 mg, 85%). The characterization data were identical to those previously reported.\(^3\)

**IR (neat):** $\tilde{\nu}$ (cm$^{-1}$) = 3059, 3027, 2973, 2926, 2869, 2255, 1642, 1597, 1494, 1445, 1349, 1306, 1237, 1125, 1026, 981, 907, 814.

$^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.66 (d, J = 8.3 Hz, 2H), 7.34-7.22 (m, 7H), 6.40 (dd, J = 8.0, 1.0 Hz, 1H), 5.38 (d, J = 8.0 Hz, 1H), 5.97 (d, J = 11.5 Hz, 1H), 3.02 (s, 2H), 3.75 (bs, 2H), 2.39 (s, 3H, H$_1$), 1.75 (s, 3H), 1.66 (s, 3H).

$^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 143.8, 134.3, 129.9, 129.4, 127.7, 124.6, 122.4, 121.0, 45.1, 21.6, 20.4, 19.7.

**Chiral HPLC analysis:** Prepared 9b by using 8b (1 equiv), (aR)-(+) -7 (3 mol%) and AgSbF$_6$ (6 mol%) in CH$_2$Cl$_2$ at –20°C for 15 h. Chiralpak AS-H, 95/5 n-heptane/i-PrOH, 1 mL/min. Retention time for minor enantiomer = 9.91 min; for major enantiomer = 11.45 min (ee = 29%); $[\alpha]_D$ = 28.9 (c 0.1, CHCl$_3$).

$\{[\alpha]_D\}$(ent-9b) = −72 (c 0.85, CHCl$_3$, ee = 52%)\(^4\)
According to the general procedure GP: using rac-7 (11 mg, 0.0108 mmol), AgSbF$_6$ (7.4 mg, 0.022 mmol) and 20 (122.2 mg, 0.36 mmol). The reaction mixture in CH$_2$Cl$_2$ (7 mL) was stirred at room temperature for 1h. Silica gel chromatography (Rf = 0.4, pentane/AcOEt, 10/1) gave 21 as a white solid (122.2 mg, quant) The characterization data were identical to those previously reported.

IR (neat): $\tilde{\nu}$ (cm$^{-1}$) = 3061, 2927, 2871, 2851, 2361, 2257, 1643, 1496, 1446, 1348, 1329, 1281, 1177, 1161, 1092, 1069, 979, 906.

$^1$H NMR (300 MHz, CDCl$_3$) $\delta$ 7.89 (d, $J = 7.7$ Hz, 1H), 7.44 (d, $J = 7.1$ Hz, 1H), 7.33-7.21 (m, 7H), 6.47 (d, $J = 7.9$ Hz, 1H), 5.39 (d, $J = 8.0$ Hz, 1H), 3.81 (d, $J = 12.0$ Hz, 1H), 3.19 (d, $J = 11.9$ Hz, 1H), 2.61 (s, 3H), 1.19 (d, $J = 4.4$ Hz, 1H), 1.02 (d, $J = 4.1$ Hz, 1H), 0.88 (s, 3H).

$^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 139.0, 137.7, 136.9, 133.1, 132.9, 130.1, 129.9, 128.6, 127.3, 126.4, 120.9, 117.6, 48.0, 40.1, 24.6, 21.0, 20.9, 19.1.

Chiral HPLC analysis: Prepared 21 by using 20 (1 equiv), (aR)-(+) -7 (3 mol%) and AgSbF$_6$ (6 mol%) in CH$_2$Cl$_2$ at $-20^\circ$C for 15 h. Chiralpak AS-H, 95/5 n-heptane/i-PrOH, 1 mL/min. Retention time for minor enantiomer = 6.46 min; for major enantiomer = 7.89 min ($ee = 32\%$); [$\alpha_D$] = 68.9 (c 0.1, CHCl$_3$).

{[$\alpha_D$] (ent-21) = $-206$ (c 1.42, CHCl$_3$, $ee = 75\%$).}

Inseparable mixture of dimethyl-5-(propan-2-ylidene)cyclopent-2-ene-1,1-dicarboxylate (a) and dimethyl 5-(propan-2-ylidene)cyclopent-3-ene-1,1-dicarboxylate (a') with a ratio (2:1) (11a,a')

According to the general procedure GP: using rac-7 (11 mg, 0.0108 mmol), AgSbF$_6$ (7.4 mg, 0.022 mmol) and 10a (85.8 mg, 0.36 mmol). The reaction mixture in CH$_2$Cl$_2$ (7 mL) was stirred at room temperature for 1h. Silica gel chromatography (Rf = 0.4, pentane/AcOEt, 10/1) gave 11a and 11a' as an inseparable mixture (2:1) of colorless oil. The characterization data were identical to those previously reported.

IR (neat): $\tilde{\nu}$ (cm$^{-1}$) = 2954, 2911, 1731, 1453, 1379, 1248, 1155, 1060, 865.

$^1$H NMR (300 MHz, CDCl$_3$) $\delta$ 5.79 (s, 1H, a), 5.72 (s, 1H, b), 5.58 (s, 1H, a), 5.37 (s, 1H, b), 3.73 (s, 6H, b), 3.71 (s, 6H, a), 3.18 (bs, 2H, b), 3.01 (bs, 2H, a), 2.64 (t, $J = 6.6$ Hz, 2H, b), 2.48-2.45 (m, 2H, a), 1.83 (s, 3H, a), 1.81 (s, 3H, b), 1.79 (s, 3H, a), 1.77 (s, 3H, b).
\^13\text{C} \text{NMR (75 MHz, CDCl}_3) \delta 172.7 \text{ (b)}, 172.1 \text{ (a)}, 146.2 \text{ (a)}, 138.9 \text{ (b)}, 138.1 \text{ (a)}, 135.8 \text{ (b)}, 125.0 \text{ (a)}, 124.5 \text{ (b)}, 120.8 \text{ (2CH, a, b), 66.1 \text{ (a)}, 59.5 \text{ (b)}, 52.9 \text{ (b)}, 52.7 \text{ (a)}, 43.4 \text{ (b)}, 40.4 \text{ (b)}, 34.9 \text{ (a)}, 32.2 \text{ (a)}, 27.5 \text{ (a)}, 27.4 \text{ (b)}, 20.0 \text{ (CH}_3 \text{, a)}, 19.9 \text{ (CH}_3 \text{, b}).

3-(2-Methoxypropan-2-yl)-4-methylene-1-tosylpyrrolidine (12)

To a solution of rac-7 (13.0 mg, 0.01 mmol, 0.03 equiv) in dry and degassed MeOH (4 mL) was added AgSbF\textsubscript{6} (2.52 mL of 0.01 M in MeOH, 0.02 mmol, 0.06 equiv). After 5 min stirring at room temperature, a solution of 10a (100 mg, 0.42 mmol, 1 equiv) in methanol (1.9 mL) (final concentration 0.05 M) was added. The mixture was stirred at room temperature. After 24 h, the mixture was filtered over a short pad of silica and washed with Et\textsubscript{2}O. The solution was concentrated under reduced pressure. Purification by flash chromatography on silica gel (Rf = 0.38, EtOAc/pentane, 1/10) afforded 12 (80 mg, 70\% yield) as colorless oil. The characterization data were identical to those previously reported.\textsuperscript{5}

IR (neat): $\tilde{\nu}$ (cm\textsuperscript{-1}) = 2953, 1733, 1434, 1364, 1272, 1230, 1202, 1077.

\textsuperscript{1}H NMR (300 MHz, CDCl\textsubscript{3}) $\delta$, 5.03 (bs, 1H), 5.00 (bs, 1H), 3.72 (s, 3H), 3.71 (s, 3H), 3.18 (s, 3H), 2.96-2.84 (m, 3H), 2.57 (dd, $J$ = 15.0, 9.0 Hz, 1H), 2.00 (dd, $J$ = 12.0, 9.0 Hz, 1H), 1.17 (s, 3H), 1.11 (s, 3H).

\textsuperscript{13}C NMR (75 MHz, CDCl\textsubscript{3}) $\delta$ 172.2, 172.1, 148.3, 110.7, 76.9, 58.7, 52.8, 49.3, 49.2, 43.5, 36.1, 22.8, 22.3.

Dimethyl 4,4-dimethyl-3a,4-dihydro-1H-cyclopenta[b]naphthalene-2,2(3\textit{H})-dicarboxylate (14)

According to the general procedure GP: using rac-7 (11 mg, 0.0108 mmol), AgSbF\textsubscript{6} (7.4 mg, 0.022 mmol) and 13 (113.2 mg, 0.36 mmol). The reaction mixture in CH\textsubscript{2}Cl\textsubscript{2} (7 mL) was stirred at room temperature for 1h. Silica gel chromatography (Rf = 0.14, pentane/AcOEt, 10/1) gave 14 as a white solid (113.2 mg, quant). The characterization data were identical to those previously reported.\textsuperscript{6}

IR (neat): $\tilde{\nu}$ (cm\textsuperscript{-1}) = 2954, 2868, 2843, 1731, 1433, 1200, 1129, 1113, 1066, 989, 888, 752.

\textsuperscript{1}H NMR (400 MHz, CDCl\textsubscript{3}) $\delta$ 7.31-7.29 (m, 1H), 7.16-7.13 (m, 2H), 7.03-7.01 (m, 1H), 6.37 (d, $J$ = 2.2 Hz, 1H), 3.78 (s, 3H), 3.73 (s, 3H), 3.32 (dd, $J$ = 18.0, 1.5 Hz, 1H), 3.01 (dt, $J$ = 18.0 Hz, 3 Hz, 1H), 2.75-2.70 (m, 1H), 2.62 (ddd, $J$ = 12.3, 7.5, 1.4 Hz, 1H), 2.17 (t, $J$ = 12.4 Hz, 1H), 1.44 (s, 3H), 0.94 (s, 3H).

\textsuperscript{13}C NMR (100 MHz, CDCl\textsubscript{3}) $\delta$ 172.2, 172.0, 144.1, 143.0, 134.0, 127.0, 126.4, 126.3, 123.5, 119.5, 59.0, 52.9, 52.9, 48.5, 39.3, 36.7, 34.9, 25.7, 22.1.
2-Methyl-1-(2-phenylcyclopropyl)prop-1-en-1-yl pivalate (16)

To a solution of rac-7 (15 mg, 14.75 mmol, 0.025 equiv) in MeNO₂ (3 mL) was added a solution of AgSbF₆ (2.52 mL of 0.01 M in MeNO₂, 0.02 mmol, 0.05 equiv) at room temperature. The mixture was stirred for 5 min. Styrene (0.27 mL, 2.38 mmol, 4 equiv) and the solution of 2-methylbut-3-ynyl pivalate 15 (99.1 mg, 0.59 mmol, 1 equiv) in MeNO₂ (final concentration = 0.05 M) was added into the mixture at room temperature. After stirring for 15 h, the mixture was filtered over a short pad of silica and washed with Et₂O, and then concentrated under reduced pressure. Purification by column chromatography on silica gel (Rf = 0.45, EtOAc/pentane, 1/20) afforded 16 as a colorless oil in a 20:1 ratio of inseparable mixture of diastereomers (97 mg, 60%). The characterization data were identical to those previously reported.⁵

IR (neat): ṽ (cm⁻¹) = 2979, 2933, 2872, 1738, 1604, 1395, 1363, 1257, 1157, 767, 697.

¹H NMR (300 MHz, CDCl₃) δ 7.30-7.18 (m, 3H), 7.05-7.02 (m, 2H), 2.32 (bt, J = 7.1 Hz, 2H), 1.53 (s, 3H), 1.46 (s, 3H), 1.29-1.28 (m, 1H), 1.27 (s, 9H), 1.05 (dd, J = 11.8 Hz, 6.3 Hz, 1H).

¹³C NMR (75 MHz, CDCl₃) δ 176.8, 139.6, 138.2, 127.6, 127.4, 125.6, 123.2, 39.0, 27.4, 24.1, 21.9, 18.7, 17.4, 11.9.

Inseparable mixture of dimethyl 7-(propan-2-ylidene)-3,3a,7a-tetrahydro-1H-indene-2,2(6H)-dicarboxylate (18) and dimethyl 3,3a,6,7-tetrahydroazulene-2,2(1H)-dicarboxylate (19)

According to the general procedure GP: using rac-7 (11 mg, 0.0108 mmol), AgSbF₆ (7.4 mg, 0.022 mmol) and 17 (100.2 mg, 0.36 mmol). The reaction mixture in CH₂Cl₂ (7 mL) was stirred at room temperature for 1h. Silica gel chromatography (Rf = 0.24, pentane/AcOEt, 10/1) gave an inseparable mixture of 18 and 19 (4:1, 67.1 mg, 67%) in favor of 18 as a colorless oil.

The characterization data were identical to those previously reported.⁷

¹H NMR (300 MHz, CDCl₃) δ 5.85-5.82(m, 1H), 5.70-5.69 (m, 1H), 5.16 (bs, 0.5H), 3.71 (m, 10H), 2.99-2.60 (m, 6H, 2.20-2.14 (bm, 3H), 1.77 (s, 3H), 1.71-1.67 (m, 1H), 1.63 (s, 3H), 0.99 (s, 1H), 0.94 (s, 1H).

Z = C(CO₂Me)₁
$^{13}$C NMR (75 MHz, CDCl$_3$) $\delta$ 173.3, 172.3, 136.7, 135.1, 132.6, 129.2, 129.1, 128.1, 124.0, 58.5, 52.8, 48.3, 44.5, 42.1, 41.1, 39.9, 39.2, 39.1, 37.6, 34.4, 31.6, 28.7, 22.1, 21.9.
3. Spectral data
Ph\_2PPh\_2PPh\_2PPh\_2Ph \quad \text{AuCl} \quad \text{PPh\_2PPh\_2Ph} \\
\begin{array}{c}
\text{n} \\
6
\end{array}
4. X-Ray crystal structure determination

Compound 3

A single crystal was selected, mounted and transferred into a cold nitrogen gas stream. Intensity data was collected with a Bruker Kappa-APEX2 system using micro-source Cu-Kα radiation. Unit-cell parameters determination, data collection strategy and integration were carried out with the Bruker APEX2 suite of programs. Multi-scan absorption correction was applied. The structure was solved with SHELXT-2014 and refined anisotropically by full-matrix least-squares methods with SHELXL-2014 using the WinGX suite. The structure was deposited at the Cambridge Crystallographic Data Centre with number CCDC 1448365 and can be obtained free of charge via www.ccdc.cam.ac.uk.

Empirical formula C40 H32 Cl4 P2 Pd
Formula weight 822.79
Temperature 200(1) K
Wavelength 1.54178 Å
Crystal system Monoclinic
Space group P 21/c
Unit cell dimensions
\[ a = 9.8924(2) \text{ Å} \quad \alpha = 90^\circ \]
\[ b = 19.0871(5) \text{ Å} \quad \beta = 100.6180(10)^\circ \]
\[ c = 19.8273(4) \text{ Å} \quad \gamma = 90^\circ \]
Volume 3679.63(14) Å³
Z 4
Density (calculated) 1.485 g.cm⁻³
Absorption coefficient 7.777 mm⁻¹
F(000) 1664
Crystal size 0.4 x 0.3 x 0.1 mm³
θ range for data collection 3.241° to 66.657°
Index ranges -11<=h<=11, -22<=k<=14, -23<=l<=23
Reflections collected 38783
Independent reflections 6496 [R(int) = 0.0256]
Completeness to θ = 66.500° 99.8 %
Absorption correction Semi-empirical from equivalents
Max. and min. transmission 0.519 and 0.152
Refinement method Full-matrix least-squares on F²
Data / restraints / parameters 6496 / 0 / 424
Goodness-of-fit on F² 1.032
Final R indices [I > 2σ(I)] R1 = 0.0263, wR2 = 0.0682
R indices (all data) R1 = 0.0271, wR2 = 0.0688
Largest difference peak and hole 0.928 and -0.671 e.Å⁻³

MeOH and HCl adducts on 3

A single crystal was selected, mounted and transferred into a cold nitrogen gas stream. Intensity data was collected with a Bruker Kappa-APEX2 system using micro-source Cu-Kα radiation. Unit-cell parameters determination, data collection strategy and integration were carried out with the Bruker APEX2 suite of programs. Multi-scan absorption correction was applied. The structure was solved with SHELXT-2014 and refined anisotropically by full-matrix least-squares methods with SHELXL-2014 using the WinGX suite. Crystal absolute structure was determined by anomalous scattering effects analysis. The structure was deposited at the Cambridge Crystallographic Data Centre with number CCDC 1448366 and can be obtained free of charge via www.ccdc.cam.ac.uk.
Empirical formula: C40.80 H35.40 Cl4.20 O0.80 P2 Pd

Formula weight: 855.72
Temperature: 200(1) K
Wavelength: 1.54178 Å
Crystal system: Monoclinic
Space group: C c
Unit cell dimensions:
\[ a = 20.1238(7) \text{ Å} \]
\[ b = 12.6403(4) \text{ Å} \]
\[ c = 17.4640(6) \text{ Å} \]
\[ \alpha = 90^\circ \]
\[ \beta = 119.991(2)^\circ \]
\[ \gamma = 90^\circ \]
Volume: 3847.5(2) Å³
Z: 4
Density (calculated): 1.477 g.cm⁻³
Absorption coefficient: 7.600 mm⁻¹
F(000): 1736
Crystal size: 0.2 x 0.2 x 0.1 mm³
θ range for data collection: 4.321° to 66.778°
Index ranges:
\[-23 \leq h \leq 23, -14 \leq k \leq 15, -20 \leq l \leq 20\]
Reflections collected: 30800
Independent reflections: 6637 [R(int) = 0.0223]
Completeness to θ = 66.500°: 100.0 %
Absorption correction: Semi-empirical from equivalents
Max. and min. transmission: 0.678 and 0.399
Refinement method: Full-matrix least-squares on F²
Data / restraints / parameters: 6637 / 2 / 460
Goodness-of-fit on F²: 1.062
Final R indices [I > 2σ(I)]: R1 = 0.0232, wR2 = 0.0603
R indices (all data): R1 = 0.0233, wR2 = 0.0605
Absolute structure parameter: -0.024(3)
Largest difference peak and hole: 0.667 and -0.527 e.Å⁻³

Compound 4

A single crystal was selected, mounted and transferred into a cold nitrogen gas stream. Intensity data was collected with a Bruker Kappa-APEX2 system using micro-source Cu-Kα radiation. Unit-cell parameters determination, data collection strategy and integration were carried out with the Bruker APEX2 suite of programs. Multi-scan absorption correction was applied. The structure was solved with SIR-92⁸ and refined anisotropically by full-matrix least-squares methods with SHELXL-2014⁹ using the WinGX suite. Crystal absolute structure was determined by anomalous scattering effects analysis. Chemical absolute configuration was then deduced.¹⁰ The structure was deposited at the Cambridge
Crystallographic Data Centre with number CCDC 1448367 and can be obtained free of charge via [www.ccdc.cam.ac.uk](http://www.ccdc.cam.ac.uk).

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<td>Wavelength</td>
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<td>Crystal system</td>
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<tr>
<td>Space group</td>
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<td>Unit cell dimensions</td>
<td>a = 9.9582(3) Å, α = 90°</td>
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<td>b = 21.3845(7) Å, β = 103.135(2)°</td>
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<td></td>
<td>c = 10.1108(3) Å, γ = 90°</td>
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<td>Density (calculated)</td>
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<td>Crystal size</td>
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<td>Independent reflections</td>
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<td>Max. and min. transmission</td>
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<td>Data / restraints / parameters</td>
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<td>Goodness-of-fit on F²</td>
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<td>Final R indices [I &gt; 2σ(I)]</td>
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<td>R indices (all data)</td>
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<tr>
<td>Absolute structure parameter</td>
<td>-0.027(5)</td>
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<td>Largest difference peak and hole</td>
<td>0.730 and -0.377 e.Å⁻³</td>
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</table>

**Compound 6**

![Compound 6 Image](image-url)
A single crystal was selected, mounted and transferred into a cold nitrogen gas stream. Intensity data was collected with a Bruker Kappa-APEX2 system using micro-source Cu-Kα radiation. Unit-cell parameters determination, data collection strategy and integration were carried out with the Bruker APEX2 suite of programs. Multi-scan absorption correction was applied. The structure was solved with SHELXT-2014 and refined anisotropically by full-matrix least-squares methods with SHELXL-2014 using the WinGX suite. The structure was deposited at the Cambridge Crystallographic Data Centre with number CCDC 1448368 and can be obtained free of charge via www.ccdc.cam.ac.uk.

**Empirical formula**  
C82 H68 Au2 Cl4 O P4

**Formula weight**  
1728.97

**Temperature**  
200(1) K

**Wavelength**  
1.54178 Å

**Crystal system**  
Triclinic

**Space group**  
P -1

**Unit cell dimensions**  
\[\begin{align*}
a &= 12.7889(5) \ \text{Å} & \alpha &= 93.515(3)^\circ \\
b &= 16.3920(6) \ \text{Å} & \beta &= 96.512(3)^\circ \\
c &= 19.0982(7) \ \text{Å} & \gamma &= 112.335(3)^\circ
\end{align*}\]

**Volume**  
3655.6(2) Å³

**Z**  
2

**Density (calculated)**  
1.571 g.cm⁻³

**Absorption coefficient**  
9.957 mm⁻¹

**F(000)**  
1708

**Crystal size**  
0.25 x 0.2 x 0.1 mm³

**θ range for data collection**  
3.773° to 66.902°

**Index ranges**  
\[-15\leq h \leq 15, \ -19\leq k \leq 19, \ -18\leq l \leq 22\]

**Reflections collected**  
71019

**Independent reflections**  
12773 [R(int) = 0.0573]

**Completeness to θ = 66.500°**  
98.9 %

**Absorption correction**  
Semi-empirical from equivalents

**Max. and min. transmission**  
0.659 and 0.270

**Refinement method**  
Full-matrix least-squares on F²

**Data / restraints / parameters**  
12773 / 96 / 874

**Goodness-of-fit on F²**  
1.132

**Final R indices [I > 2σ(I)]**  
R1 = 0.0603, wR2 = 0.1429

**R indices (all data)**  
R1 = 0.0818, wR2 = 0.1610

**Largest difference peak and hole**  
2.920 and -1.575 e.Å⁻³

---

**Compound rac-7**

A single crystal was selected, mounted and transferred into a cold nitrogen gas stream. Intensity data was collected with a Bruker Kappa-APEX2 system using fine-focus sealed tube Mo-Kα radiation. Unit-cell parameters determination, data collection strategy and integration were carried out with the Bruker APEX2 suite of programs. Multi-scan absorption correction was applied. The structure was solved with SIR-92 and refined anisotropically by full-matrix least-squares methods with SHELXL-2014 using the WinGX suite. The structure was deposited at the Cambridge Crystallographic Data Centre with number CCDC 1448369 and can be obtained free of charge via www.ccdc.cam.ac.uk.
<table>
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<td>Temperature</td>
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<td>Wavelength</td>
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<td>Crystal system</td>
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<tr>
<td>Space group</td>
<td>P 21/n</td>
<td></td>
</tr>
</tbody>
</table>
| Unit cell dimensions              | a = 12.6409(3) Å  \(\alpha = 90^\circ\)  
b = 16.9730(4) Å  \(\beta = 104.6610(10)^\circ\)  
c = 18.0808(5) Å  \(\gamma = 90^\circ\)  |
| Volume                            | 3753.00(16) Å \(^3\) |
| Z                                 | 4 |
| Density (calculated)              | 1.965 g.cm\(^{-3}\) |
| Absorption coefficient            | 8.208 mm\(^{-1}\) |
| F(000)                            | 2112 |
| Crystal size                      | 0.5 x 0.2 x 0.15 mm\(^3\) |
| \(\theta\) range for data collection | 2.053° to 30.533° |
| Index ranges                      | \(-18\leq h\leq18, -24\leq k\leq24, -25\leq l\leq25\) |
| Reflections collected             | 55873 |
| Independent reflections           | 11469 [R(int) = 0.0200] |
| Completeness to \(\theta = 25.242^\circ\) | 100.0 % |
| Absorption correction             | Semi-empirical from equivalents |
| Max. and min. transmission        | 0.419 and 0.165 |
| Refinement method                 | Full-matrix least-squares on \(F^2\) |
| Data / restraints / parameters     | 11469 / 0 / 433 |
| Goodness-of-fit on \(F^2\)        | 1.083 |
| Final R indices [I > 2\(\sigma(I)\)] | R1 = 0.0191, wR2 = 0.0439 |
| R indices (all data)              | R1 = 0.0248, wR2 = 0.0462 |
| Largest difference peak and hole   | 0.791 and -0.979 e.Å \(^3\) |

**Compound aR-(+)-7**

A single crystal was selected, mounted and transferred into a cold nitrogen gas stream. Intensity data was collected with a Bruker Kappa-APEX2 system using micro-source Cu-K\(\alpha\) radiation. Unit-cell parameters determination, data collection strategy and integration were carried out with the Bruker APEX2 suite of programs. Multi-scan absorption correction was applied.\(^8\) The structure was solved with SIR-92\(^12\) and refined anisotropically by full-matrix least-squares methods with SHELXL-2014\(^9\) using the WinGX suite.\(^10\) Crystal absolute structure was determined by anomalous scattering effects analysis. Chemical absolute configuration was then deduced.\(^11\) The structure was deposited at the Cambridge Crystallographic Data Centre with number CCDC 1448370 and can be obtained free of charge via www.ccdc.cam.ac.uk.

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<td>Unit cell dimensions</td>
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A single crystal was selected, mounted and transferred into a cold nitrogen gas stream. Intensity data was collected with a Bruker Kappa-APEX2 system using micro-source Cu-Kα radiation. Unit-cell parameters determination, data collection strategy and integration were carried out with the Bruker APEX2 suite of programs. Multi-scan absorption correction was applied. The structure was solved with SIR-92 and refined anisotropically by full-matrix least-squares methods with SHELXL-2014 using the WinGX suite. Crystal absolute structure was determined by anomalous scattering effects analysis. Chemical absolute configuration was then deduced. The structure was deposited at the Cambridge Crystallographic Data Centre with number CCDC 1448371 and can be obtained free of charge via www.ccdc.cam.ac.uk.
5. Chiral HPLC analyses

The enantiomers of complex (7) are separated by analytical chiral chromatography, on Chiralpak IE column with an enantioselectivity of 1.52 and a resolution of 2.94. The first eluted enantiomer has a negative CD sign at 254 nm in the ternary mixture heptane / 2-PrOH / chloroform (5/2/3) used as mobile phase. A preparative separation on 1 cm diameter column allowed the collection of 200 mg of each enantiomer with ees higher than 98%, after 150 successive injections. Retention times Rt in minutes, retention factors $k_i = (Rt_i - Rt_0)/Rt_0$, enantioselectivity factor $\alpha = k_2/k_1$ and resolution $Rs = 2 (Rt_2 - Rt_1) / (w_1 + w_2)$ are given. Rt$_0$ was determined by injection of tri-tertio-butyl benzene and $w_i$ was the width of the peak.

Analytical chiral HPLC separation for compound rac-7

- The sample is dissolved in chloroform, injected on the chiral columns, and detected with an UV detector at 254 nm and circular dichroism detector at 254 nm. The flow-rate is 1 mL/min.
Semi-preparative separation for compound *rac-7*:

- Sample preparation: about 577 mg of compound *rac-7* are dissolved in 33 mL of chloroform.

- Chromatographic conditions: Chiralpak IE (250 x 10 mm), hexane / 2-PrOH / Chloroform (5/2/3) as mobile phase, flow-rate = 5 mL/min, UV detection at 254 nm.

- Injections: 150 times 220 µL, every 4.5 minutes.

- First fraction: 257 mg of the first eluted ((-, CD 254nm)-enantiomer) with ee > 98.5%

- Second fraction: 207 mg of the second eluted ((+, CD 254nm)-enantiomer) with ee > 99.5%
- Chromatograms of the collected fractions:

![Chromatograms](image)

<table>
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<tr>
<th>Retention Time</th>
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<th>Area %</th>
<th>Capacity factor</th>
<th>Relative RI</th>
<th>Resolution (USP)</th>
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Chromatograms for 9b

Chromatogram recorded on a CO$_2$ supercritical HPLC using AD-H column, with a debit of 5 mL/min and 8 % MeOH as eluant at $\lambda = 220$ nm. (±)-6-methyl-1-phenyl-3-(p-tolylsulfonyl)-3-azabicyclo[4.1.0]hept-4-ene was obtained.
Sample name: Vmav473
Column: Chiraldar AS-H
Temperature: 25 degrees
Mobile phase: Heptane/isopropanol (95/5), 1 mL/min

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Signal: DAD1 B, Sig-220,4 Ref-off

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Injection volume: 10.000
Analysis method: 1-5-CD254NM-RAVMAV441-AS-HLM
Last changed: 11/10/2014 2:16:06 PM
Location: Vial 20
Column void time (min) 2.550

Plateforme de chromatographie chirale - Aix Marseille Université
Chromatograms for 21

Chromatogram recorded on a CO₂ supercritical HPLC using OD-H column, with a debit of 5 mL/min and 8 % MeOH as eluant at \( \lambda = 220 \) nm. \((\pm)-6\)-methyl-1-phenyl-3-(o-tolylsulfonyl)-3-azabicyclo[4.1.0]hept-4-ene was obtained.

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Chiral HPLC report

Data file: C:\CHEMS\DATA\FENSTERBANK\MESURES-NOV-2014
VMAVS20_JC2.1.D
Injection date: 11/8/2014 2:43:29 PM
Avg. method: 1-5-CD254NM-20MIN.M
Last changed: 11/10/2014 6:16:28 PM
Column void time (min) 2.950

Injection volume: 10.000
Analysis method: 1-5-CD254NM-RAFC7600-LUXC2.M
Location: Vial 14
6. MS of bridged gold complex

Chloride bridged-(1,3-diphenylpropa-1,2-diene-1,3-diyl)-bis(gold(I) diphenylphosphine)

A solution of 1 (20 mg, 0.02 mmol, 1 equiv) and AgSbF₆ (6.8 mg, 0.02 mmol, 1 equiv) in CD₂Cl₂ (0.4 mL) was stirred for 3 h. The mixture was concentrated under reduced pressure to obtain the bridge gold complex (20 mg, quant). as a brown solid. (Note: This product cannot be characterized by NMR analysis)

**MS (ESI)** calcld for C₃₉H₃₀Au₂ClP₂Sb 989.1, found 989.2

7. References


