

SUPPORTING INFORMATION

Gold(I) Complexes with a Phosphinine Ligand: Synthesis and Structural Characterization

Jamal Moussa,* Lise-Marie Chamoreau and Hani Amouri*

General procedures.

All experimental manipulations were carried out under an argon atmosphere by using Schlenk tube techniques. Solvents were dried and distilled under argon by standard procedures. All reagents obtained from commercial sources were used as received. *2,6-diphenyl-4-methylphosphorin* was prepared according to a slightly modified literature procedure.¹ The ¹H, ¹³C and ³¹P NMR spectra were recorded in CD₂Cl₂ using a Bruker Avance 300 NMR spectrometer at 300.13 MHz, 75.47 and 121.45 MHz respectively. IR spectra were recorded on a Bruker Tensor 27 equipped with an ATR Harricks apparatus. UV-Vis. spectra were recorded on a JASCO V-670 Spectrophotometer. Photoluminescence spectra were recorded using a JASCO J-815 CD Spectrometer.

Synthesis of [AuCl(L_p)] (2):

A pale yellow solution of the ligand *2,6-diphenyl-4-methylphosphorin* ligand **L_p** (40 mg, 0.15 mmol) in dichloromethane (10 mL) was added to a colorless solution of [AuCl(*tht*)] (50 mg, 0.14 mmol) in dichloromethane (10 mL). The resulting pale yellow solution was stirred for 2 hours at room temperature. Then solvent volume was reduced under reduced pressure to c.a. 3 mL and addition of diethyl ether (25 mL) provided a white microcrystalline solid that was washed with two more portions of diethyl ether (15 mL each). The resulting white solid was redissolved in dichloromethane (20 mL) and filtered through celite. Evaporation of dichloromethane under reduced pressure provided [AuCl(**L_p**)] (**2**) (62 mg, 0.13 mmol) as a white microcrystalline solid. Yield: 90%. Anal. Calcd. (%) for C₁₈H₁₅AuClP·½CH₂Cl₂ (537.2 g.mol⁻¹): C 41.37, H 3.00; found: C 41.95, H 3.01. ¹H NMR (300.13 MHz, CD₂Cl₂): δ = 8.14 (d, 2 H, ³J_{H-P} = 21.9 Hz, H₃+H₅), 7.74 (m, 4 H, Phenyl), 7.55 (m, 6 H, Phenyl), 2.66 (d, 3 H, ⁵J_{H-P} = 6.9 Hz, CH₃) ppm. ¹³C{¹H} NMR (75.45 MHz, CD₂Cl₂): δ = 25.0 (d, ⁴J_{C-P} = 5.0 Hz, CH₃), 129.5 (d, ²J_{C-P} = 12.1 Hz, C₃+C₅), 130.2 (s, Ph), 130.3 (s, Ph), 130.4 (s, Ph), 139.3 (d, ²J_{C-P} = 10.0 Hz, C_{ipso}-Ph), 139.9 (d, ³J_{C-P} = 11.9 Hz, C₄), 142.7 (d, ¹J_{C-P} = 27.5 Hz, C₂+C₆) ppm. ³¹P{¹H} NMR (121.47 MHz, CD₂Cl₂): δ = 149.3 (P-Au) ppm. IR (ATR): ν = 3046, 1563, 1488, 1447, 1426, 1386, 1372, 1340, 1314, 1162, 1079, 1030, 998, 969, 874, 848, 781, 751, 697, 600, 586, 545, 492, 463, 407, 334, 254, 229, 209 cm⁻¹.

Synthesis of [Au(L_p)₂](OTf) (3):

A pale yellow solution of the ligand *2,6-diphenyl-4-methylphosphorin* ligand **L_p** (40 mg, 0.15 mmol) in dichloromethane (10 mL) was added to a colourless solution of [AuCl(*tht*)] (25 mg, 0.07 mmol) in dichloromethane (5 mL). The resulting pale yellow solution was stirred for 1 hour at room temperature and was added to a suspension of AgCF₃SO₃ (18 mg, 0.07 mmol) in dichloromethane (5 mL), stirring was maintained for 3 hours and the resulting precipitated AgCl was filtered off through

¹ G. Märkl, *Angew. Chem. Int. Ed. Engl.*, 1966, **5**, 846-847

celite. Then solvent volume of the filtrate was reduced under reduced pressure to c.a. 2 mL and addition of diethyl ether (20 mL) provided a light yellow microcrystalline solid that was washed with two more portions of diethyl ether (15 mL each). The resulting solid was identified as $[\text{Au}(\text{Lp})_2](\text{OTf})$ (**3**) (51 mg, 0.059 mmol). Yield: 84%. Anal. Calcd. (%) for $\text{C}_{37}\text{H}_{30}\text{AuF}_3\text{O}_3\text{P}_2\text{S}$ ($870.1 \text{ g}\cdot\text{mol}^{-1}$): C 51.05, H 3.47; found: C 51.16, H 3.71. ^1H NMR (300.13 MHz, CD_2Cl_2): δ = 8.05 (d, 2 H, $^3J_{\text{H-P}}$ = 20.1 Hz, H_3+H_5), 7.51-7.32 (m, 10 H, Phenyl), 2.65 (d, 3 H, $^5J_{\text{H-P}}$ = 6.6 Hz, CH_3) ppm. $^{13}\text{C}\{^1\text{H}\}$ NMR (75.45 MHz, CD_2Cl_2): δ = 25.1 (d, $^4J_{\text{C-P}}$ = 3.8 Hz, CH_3), 128.9 (d, $^2J_{\text{C-P}}$ = 12.8 Hz, C_3+C_5), 130.2 (s, Ph), 130.3 (s, Ph) 130.5 (s, Ph), 137.6 (d, $^2J_{\text{C-P}}$ = 12.7 Hz, $\text{C}_{\text{ipso}}\text{-Ph}$), 141.2 (d, $^3J_{\text{C-P}}$ = 16.6 Hz, C_4), 145.1 (d, $^1J_{\text{C-P}}$ = 21.9 Hz, C_2+C_6) ppm. $^{31}\text{P}\{^1\text{H}\}$ NMR (121.47 MHz, CD_2Cl_2): δ = 160.5 (P-Au) ppm. IR (ATR): ν = 3055, 1568, 1491, 1446, 1426, 1385, 1289, 1219 1167, 1077, 1021, 967, 873, 761, 744, 697, 628, 605, 573, 549, 515, 464, 407, 336, 313, 269, 259, 233, 204 cm^{-1} .

Tables and Figures.

Table S1. Experimental crystallographic data for $[\text{AuCl}(\text{Lp})]$ (**2**).

Empirical formula	$\text{C}_{18}\text{H}_{15}\text{AuClP}$
Formula weight	494.71 g/mol
Temperature	200(2) K
Wavelength	0.71073 Å
Crystal system	Orthorhombic
Space group	P nma
Unit cell dimensions	a = 24.7714(11) Å b = 17.0229(7) Å c = 7.5234(3) Å
	$\alpha = 90^\circ$ $\beta = 90^\circ$ $\gamma = 90^\circ$
Volume	3172.5(2) Å ³
Z	8
Density (calculated)	2.071 Mg/m ³
Absorption coefficient	9.533 mm ⁻¹
F(000)	1872
Reflections collected	19125
Independent reflections	4586, [R(int) = 0.0165]
Final R indices [I>2sigma(I)]	R1 = 0.0141, wR2 = 0.0297
Goodness-of-fit on F2	0.906
Largest diff. peak and hole (e.Å ⁻³)	0.529 and -0.993

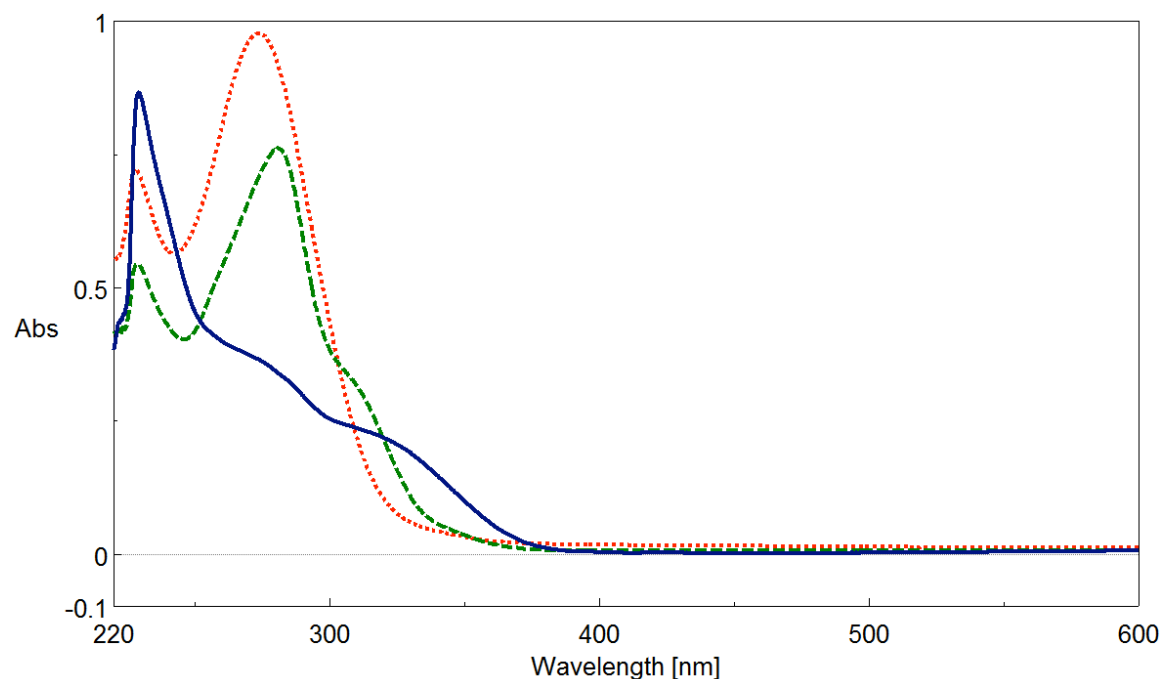


Figure S1. (a) UV-Vis. Absorption spectra in CH_2Cl_2 solutions of ligand $\mathbf{L_p}$ (red dotted line), complex $[\text{AuCl}(\mathbf{L_p})]$ (**2**) (green dashed line) and complex $[\text{Au}(\mathbf{L_p})_2](\text{OTf})$ (**3**) (blue line).

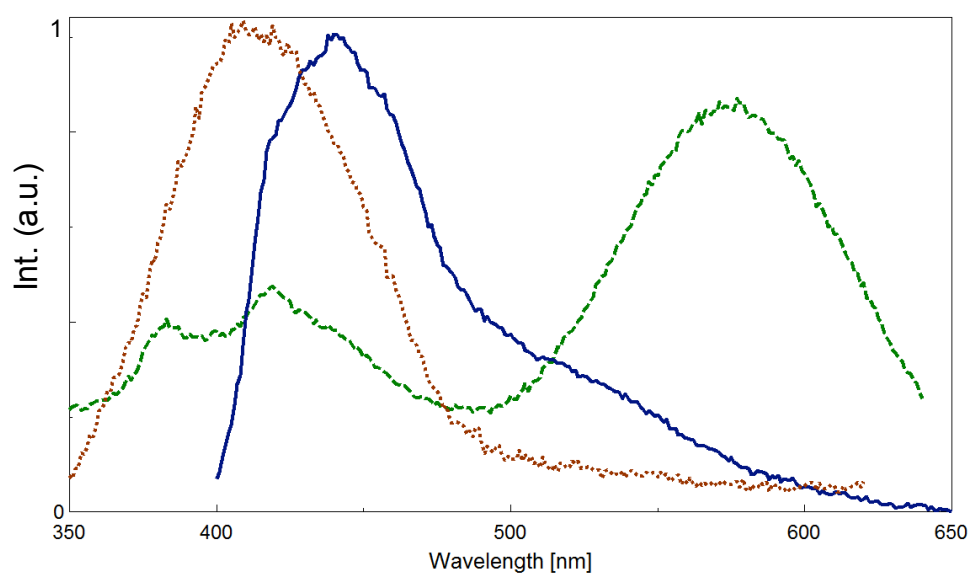


Figure S2. Photoluminescence spectra in PS thin films (2% w/w) of ligand $\mathbf{L_p}$ (red dotted line) ($\lambda_{\text{ex}}=320$ nm), complex $[\text{AuCl}(\mathbf{L_p})]$ (**2**) (green dashed line) and complex $[\text{Au}(\mathbf{L_p})_2](\text{OTf})$ (**3**) (blue line) ($\lambda_{\text{ex}}=330$ nm).

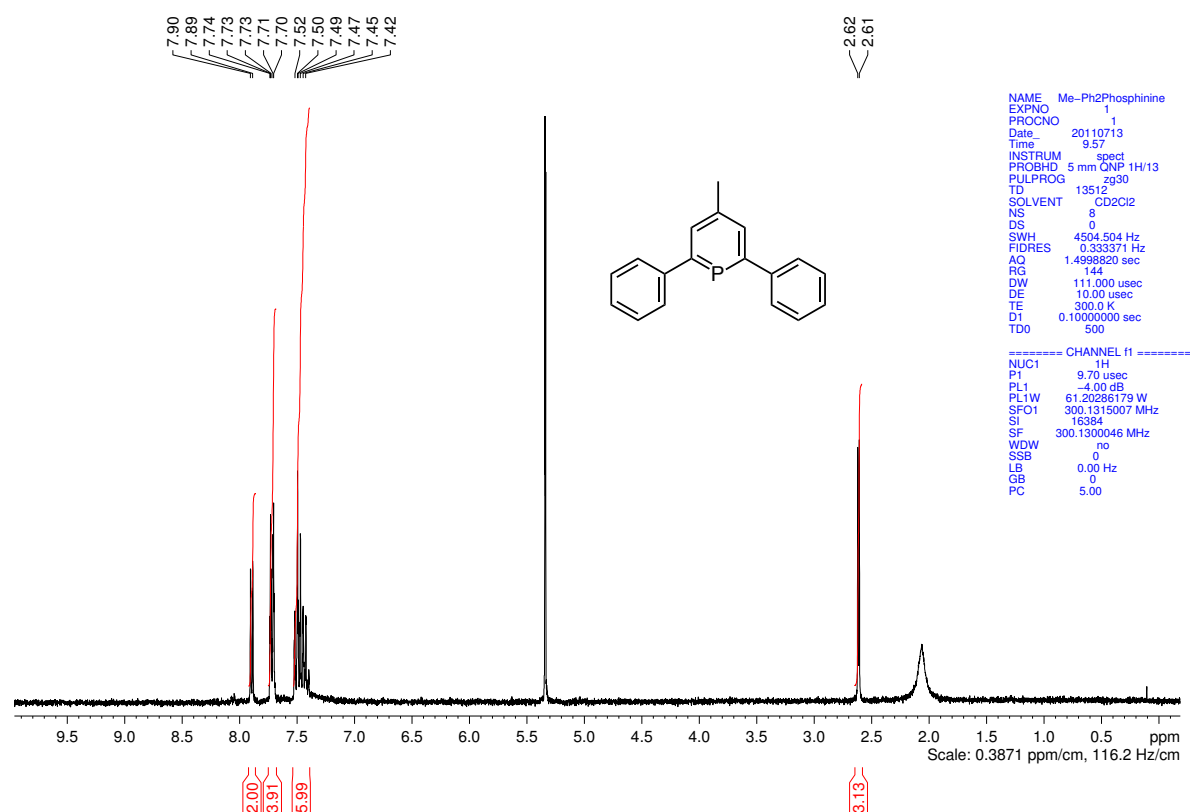


Figure S3. ¹H NMR spectrum of ligand **L_p** in CD₂Cl₂.

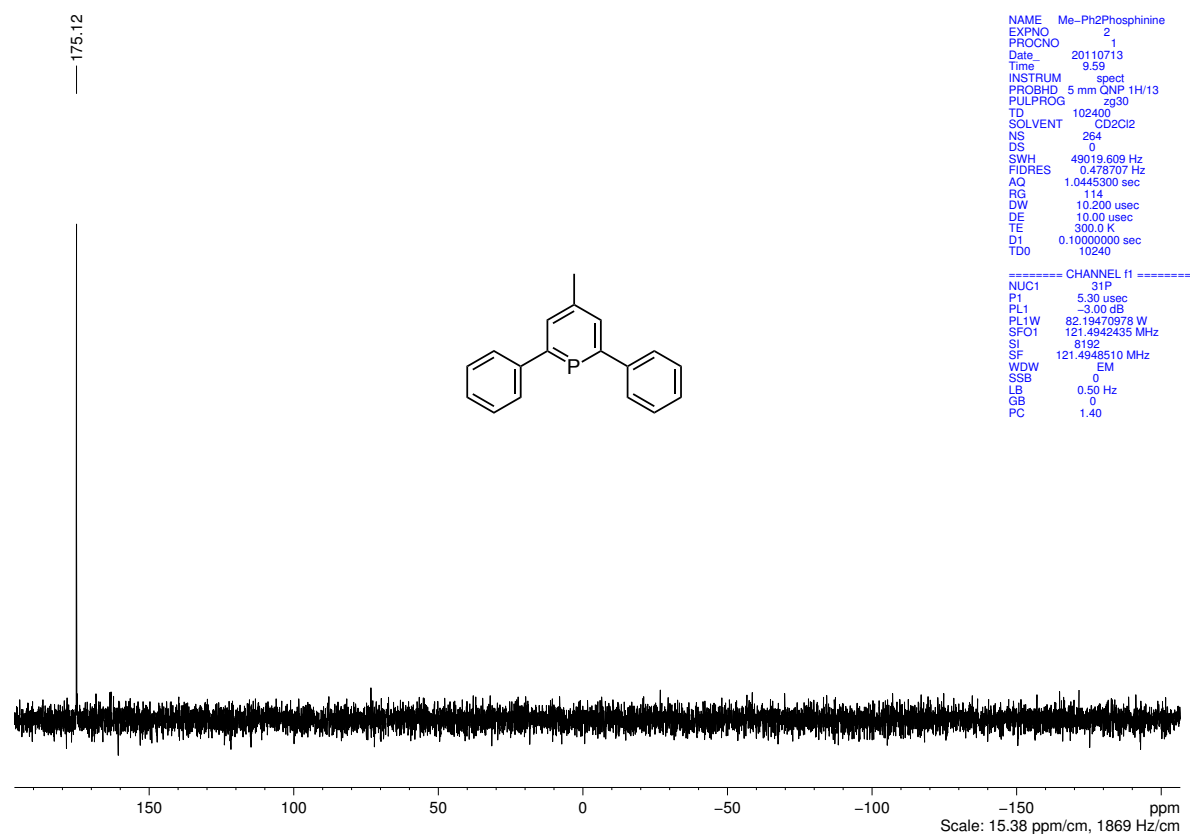


Figure S4. ³¹P NMR spectrum of ligand **L_p** in CD₂Cl₂.

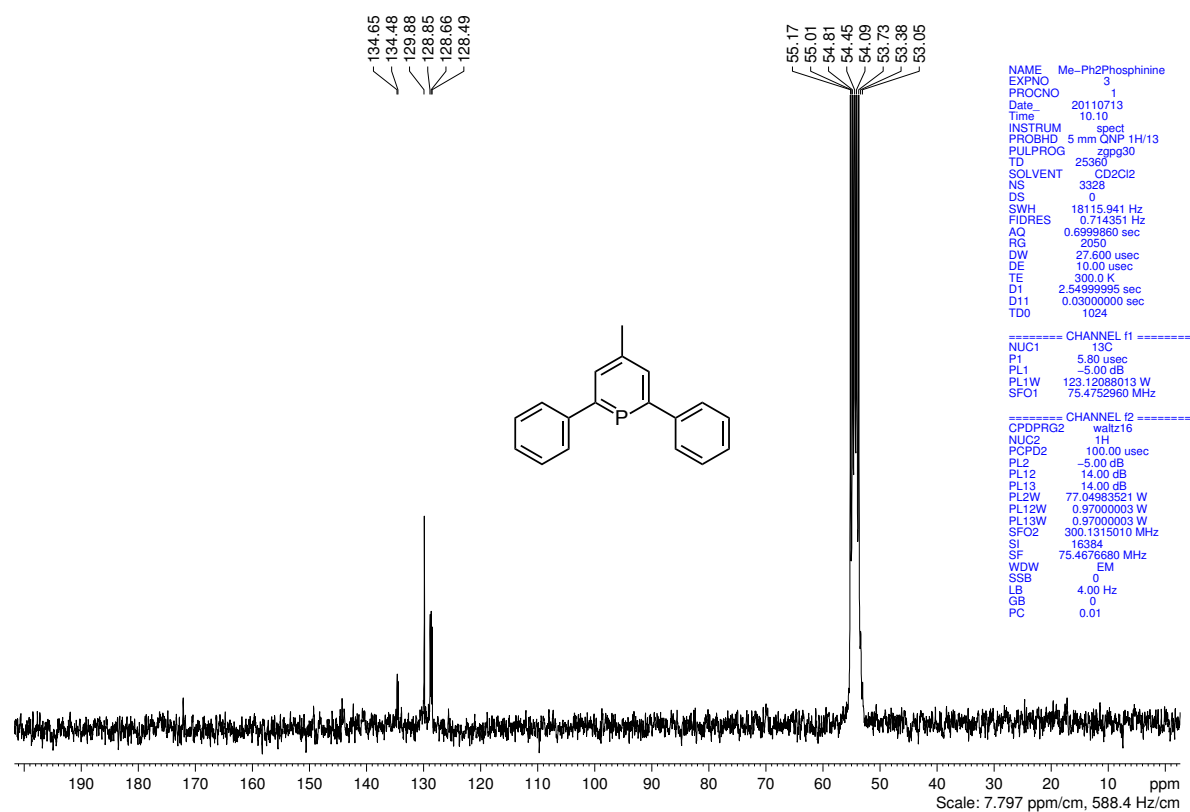


Figure S5. ^{13}C NMR spectrum of ligand **L_p** in CD_2Cl_2 .

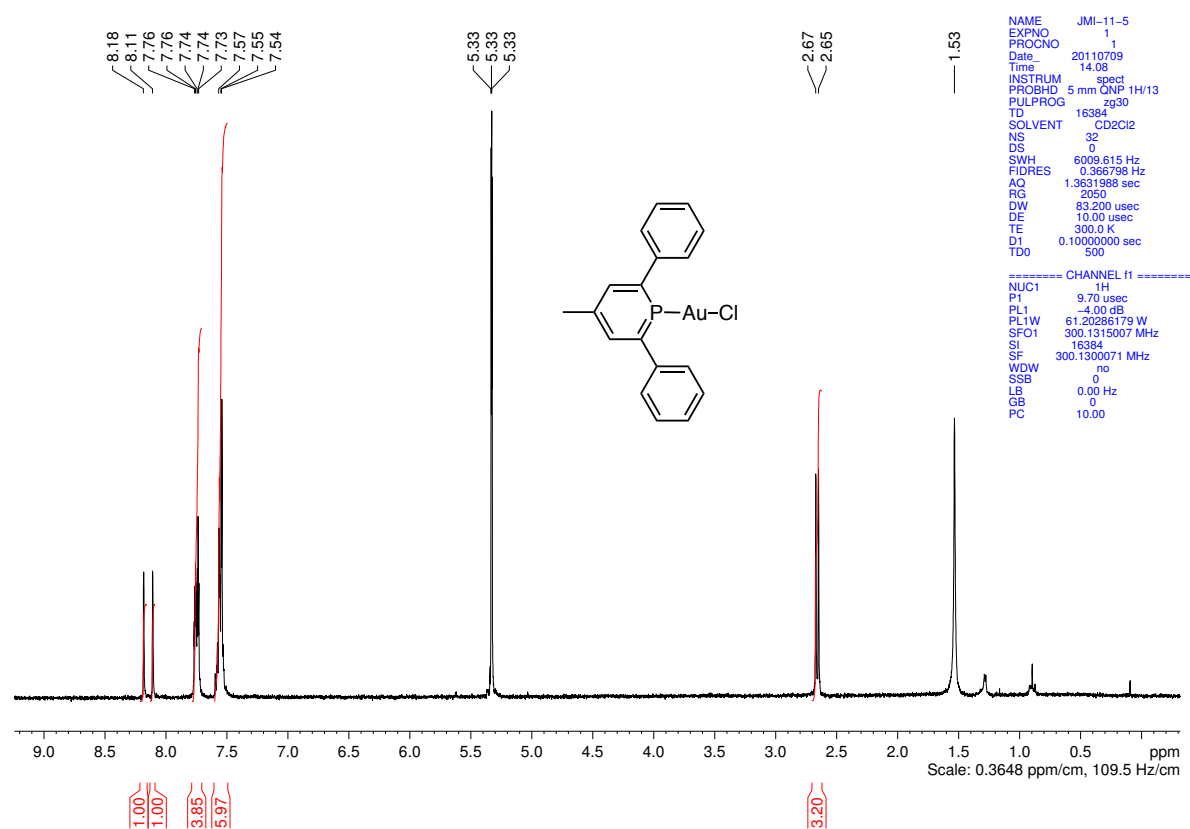


Figure S6. ^1H NMR spectrum of complex $[\text{AuCl}(\text{L}_p)]$ (**2**) in CD_2Cl_2 .

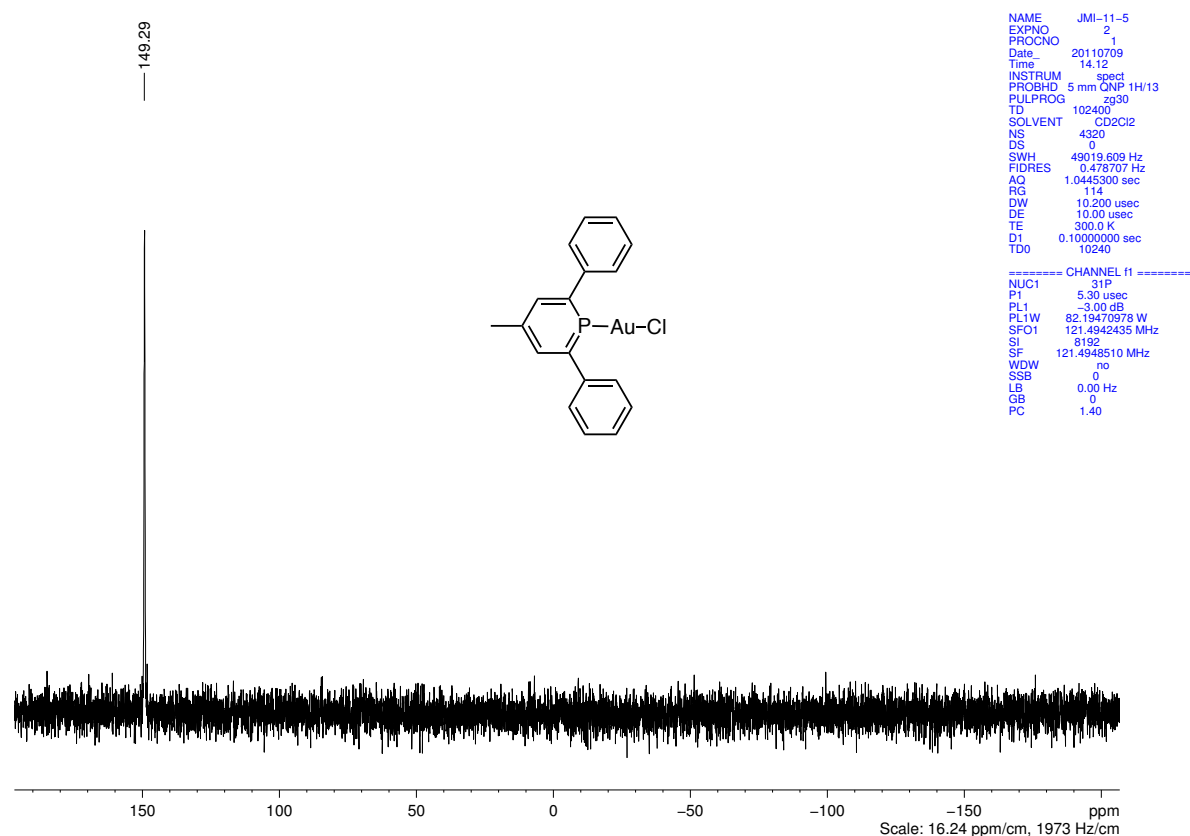


Figure S7. $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum of complex $[\text{AuCl}(\text{L}_p)]$ (**2**) in CD_2Cl_2 .

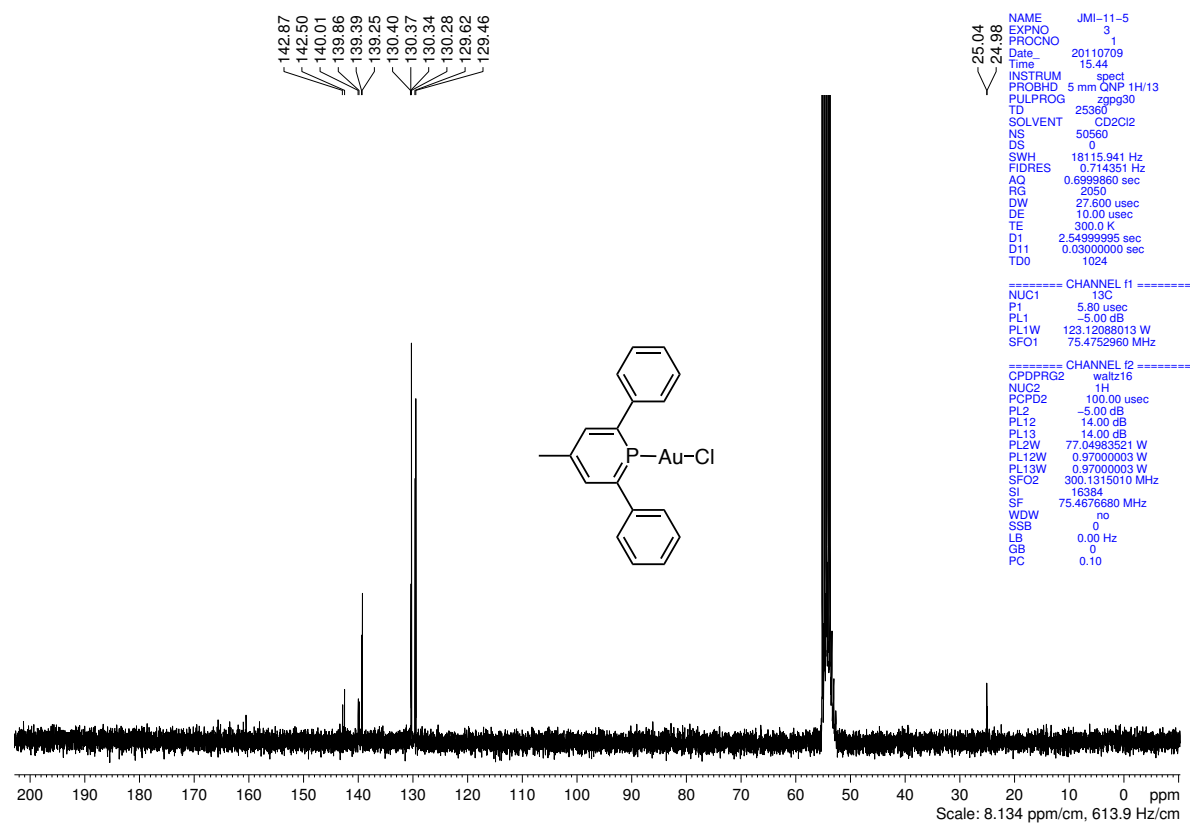


Figure S8. $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of complex $[\text{AuCl}(\text{L}_p)]$ (**2**) in CD_2Cl_2 .

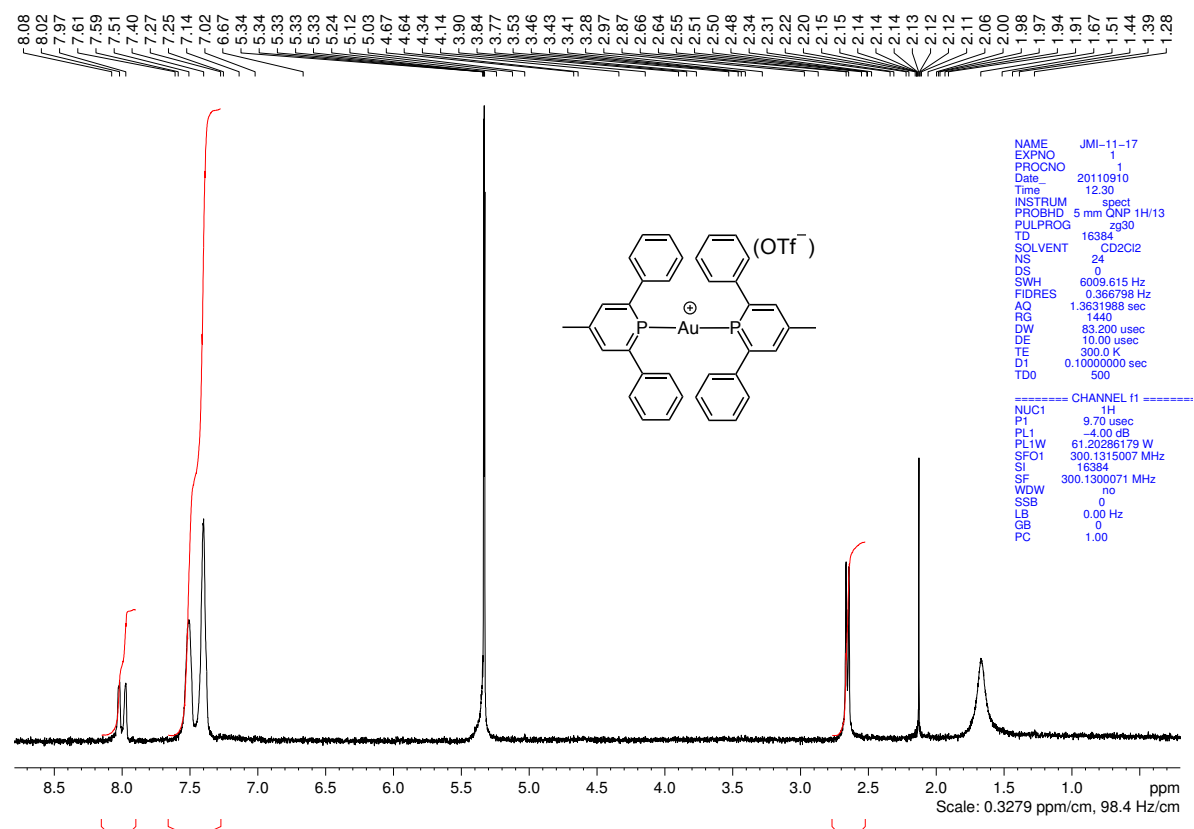


Figure S9. ¹H NMR spectrum of complex $[\text{Au}(\text{L}_p)_2](\text{OTf})$ (3) in CD₂Cl₂.

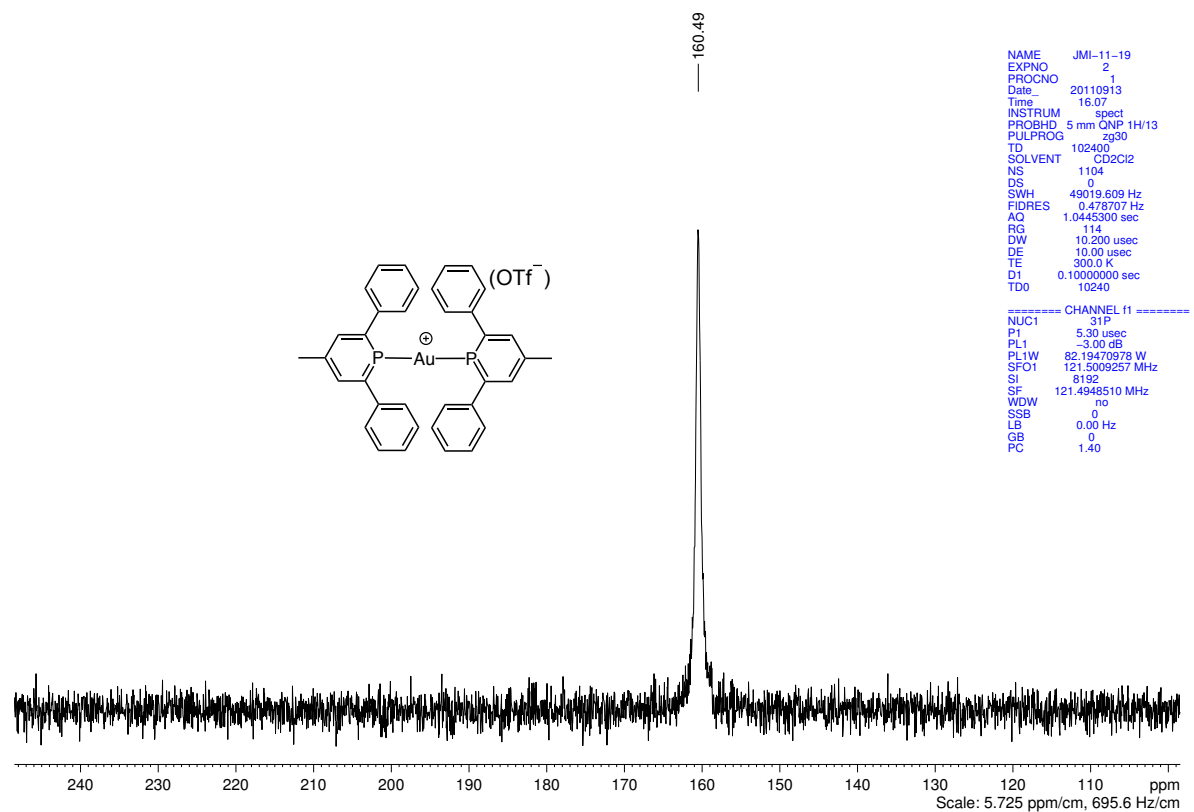


Figure S10. ³¹P{¹H} NMR spectrum of complex $[\text{Au}(\text{L}_p)_2](\text{OTf})$ (3) in CD₂Cl₂.

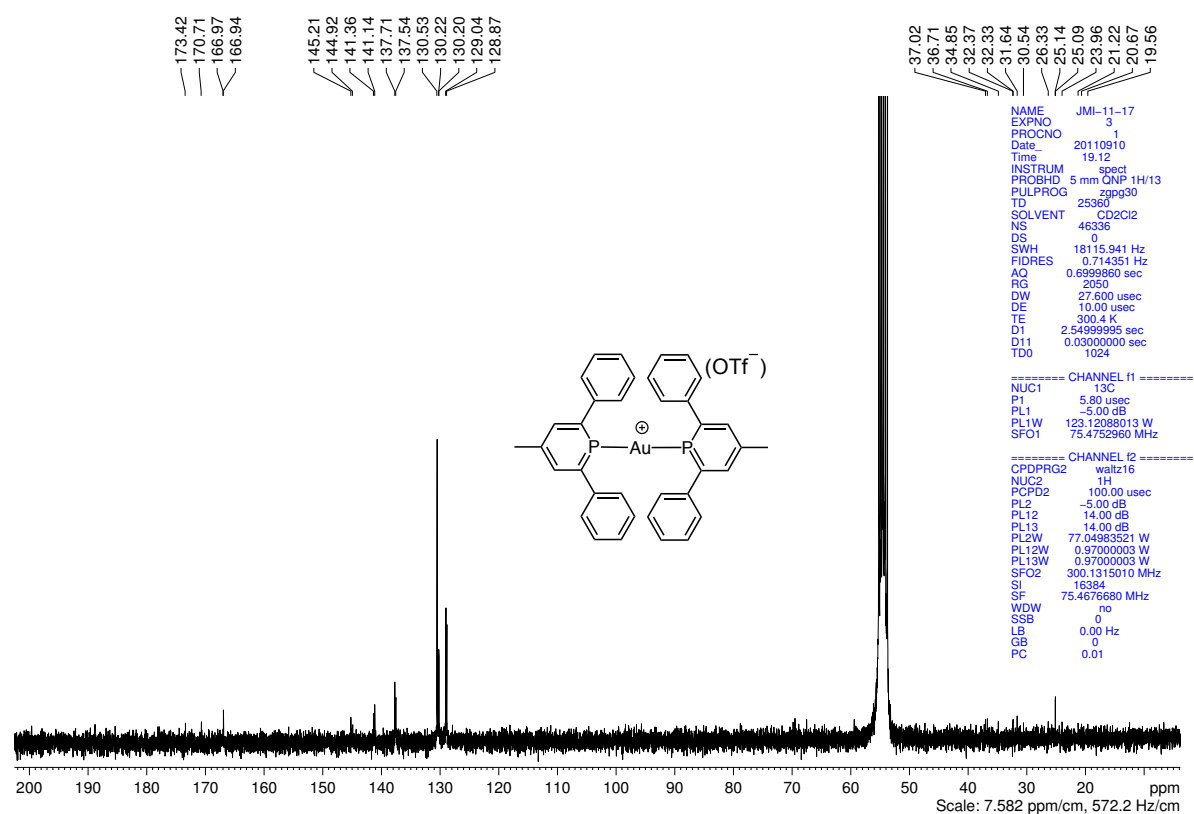


Figure S11. ¹³C{¹H} NMR spectrum of complex $[\text{Au}(\text{L}_p)_2](\text{OTf})$ (3) in CD_2Cl_2 .