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Efficient one-pot synthesis of diphenyl(pyrazin-2-yl)phosphine and its Ag^{I}, Au^{I} and Pt^{II} complexes

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§1. General remarks

Triphenylphosphine (99%), 2-chloropyrimidine (98+%), 2-chloropyrazine (98%) and lithium were used as purchased (Merk, Acros Organics). The solvents prior to use were purified by common protocols. Complexes $Pt(COD)Cl_2$ [E. Costa, P.G. Pringle, M. Ravetz, *Inorg. Synth.*, 1997, **31**, 284] and Au(tht)Cl [R. Uson, A. Laguna, M. Laguna, D. A. Briggs, H. H. Murray, J. P. Fackler, *Inorg. Synth.*, 1989, **26**, 85] were prepared as described. ^{1}H, $^{13}C\{^{1}H\}$ and $^{31}P\{^{1}H\}$ NMR spectra were recorded using a Bruker AV-500 spectrometer at 500.13, 125.8 and 202.47 MHz, respectively. The ^{1}H and ^{13}C NMR shifts were assigned using solvent peaks as reference. The $^{31}P\{^{1}H\}$ NMR shifts are expressed with respect to 85% H_3PO_4/D_2O as an external standard. Thermogravimetric analyses were carried out in a closed Al_2O_3 pan under helium flow at 10 °C/min heating rate using a Netzsch STA 449 F1 Jupiter STA. FT-IR spectra were recorded on a Bruker Vertex 80 spectrometer. The microanalyses were performed on a MICRO cube analyzer.

§2. Synthesis and characterization data

Synthesis of diphenyl(diazin-2-yl)phosphines. To a solution of triphenylphosphine (13.0 g, 0.05 mol) in absolute THF (50 ml), pieces of lithium metal (1.20 g, 0.176 mol) were added, and the mixture was stirred at room temperature for 5 h. Hereupon, Me_3SiCl (5.40 g, 0.05 mol) was added on stirring, and this was kept for 10 min. The mixture was cooled down to –20 °C, and suspension of 2-chloropyrazine or 2-chloropyrimidine (5.70 g, 0.05 mol) in THF (15 ml) was added dropwise. The resulting mixture was warmed to room temperature and stirred for 3 h. Water (50 ml) was added and the quenched mixture was extracted with CH_2Cl_2 (3 x 30 ml). The organic extracts were washed with H_2O, dried with $MgSO_4$ and evaporated in vacuum. The crude product obtained was recrystallized from $MeOH/CH_2Cl_2$ (5:1, v/v) to give colorless crystals of product **1** or **2**.

*Diphenyl(pyrazin-2-yl)phosphine **1*** Yield: 3.0 g (20%). ^{1}H NMR (500.13 MHz, $CDCl_3$, 23 °C) δ 8.69 ($C^{3}H$ in Pyr, t, J = 1.95 Hz, 1H) 8.46 ($C^{6}H$ in Pyr, q, J = 1.2, 1.2 Hz, 1H), 8.37 ($C^{5}H$ in Pyr, s, 1H), 7.38-7.50 (Ph, m, 10H). $^{31}P\{^{1}H\}$ NMR δ (202.47 MHz, CH_2Cl_2, 23 °C) -8.13. $^{13}C\{^{1}H\}$ NMR (125.8 MHz, CH_2Cl_2) δ 160.3 (C^{2} in Pyr, d, J = 5.5 Hz) 148.4 (C^{3} in Pyr, d, J = 19.5 Hz), 145.1 (C^{5} in Pyr, d, J = 8.0 Hz), 143.0 (C^{6} in Pyr, s), 134.7 (*ipso*-Ph, d, J = 9.5 Hz), 134.3 (*o*-Ph, d, J = 20.5 Hz), 129.5 (*p*-Ph, s), 128.9 (*m*-Ph d, J = 7.5 Hz).

*Diphenyl(pyrimidin-2-yl)phosphine **2*** Yield: 4.7 g (36%)**..** ^{1}H NMR (500.13 MHz, $CDCl_3$, 23 °C) δ 8.70 (d, *J* = 4.9 Hz, 2H), 7.53 (m, 4H), 7.38 (m, 6H), 7.11 (td, *J* = 4.9, 0.9 Hz, 1H). $^{31}P\{^{1}H\}$ NMR δ (202.47 MHz, CH_2Cl_2, 23 °C) 1.79. $^{13}C\{^{1}H\}$ NMR (125.8 MHz, CH_2Cl_2) δ 176.7 (C^2 in Pym, d, *J* = 12.0 Hz), 156.4 ($C^{4,6}$ in Pym, d, *J* = 6.2 Hz), 135.7 (*ipso*-Ph, d, *J* = 7.9 Hz), 134.7 (*o*-Ph, d, *J* = 20.0 Hz), 129.1 (*p*-Ph, s), 128.9 (*m*-Ph d, *J* = 7.7 Hz), 118.9 (C^5 in Pym, d, *J* = 1.5 Hz).

Besides, an additional amount of diphenyl(pyrimidin-2-yl)phosphine oxide **3** has been isolated from a mother liquor (that remained after recrystallization of **2** from MeOH/CH_2Cl_2), containing products **2** and **3** along with diphenylphosphine oxide (^{31}P NMR data). Thus, to a mother liquor in acetone (50 ml), 30% aqueous H_2O_2 (2 ml) was added at room temperature. After stirring for 20 min, the mixture was treated with aqueous KOH·0.5H_2O solution (1.0 g in 20 ml of H_2O) and extracted with CH_2Cl_2 (3 x 30 ml), then the organic layer was washed with aqueous KOH solution (0.5 g in 20 ml of H_2O) and dried over $MgSO_4$ to give colorless powder of **3**. Yield: 1.4 g (10%, based on Ph_3P). ^{1}H NMR (500.13 MHz, $CDCl_3$, 23 °C) δ 8.87 ($C^{4,6}$H in Pym, dd, *J* = 4.8, 2.0 Hz, 2H), 7.90 (*o*-Ph, t, *J* = 10 Hz, 4H), 7.50 (*p*-, *m*-Ph, m, 2H), 7.43 (*p*-, *m*-Ph, m, 4H), 7.35 (C_5H in Pym). $^{31}P\{^{1}H\}$ NMR (202.47 MHz, $CDCl_3$, 23 °C) 20.93. $^{13}C\{^{1}H\}$ (125.8 MHz, $CDCl_3$, 23 °C) δ 168.0 (C^2 in Pym, d, *J* = 159.1 Hz), 157.0 ($C^{4,6}$ in Pym, d, *J* = 13.8 Hz), 132.3 (*o*-Ph, d, *J* = 9.6 Hz), 132.1 (*p*-, *m*-Ph, d, *J* = 2.7 Hz), 131.1 (*ipso*-Ph, d, *J* = 105.1 Hz), 128.4 (*p*-, *m*-Ph, d, *J* = 12.3 Hz), 121.9 (C^5 in Pym, s).

*Synthesis of [Ag_4Cl_4(**1**)$_4$]* Silver chloride (56 mg, 0.39 mmol) was dissolved in a solution of **1** (100 mg, 0.38 mmol) in CH_2Cl_2 (1 ml). The suspension was then diluted with DMF (2 ml) and stirred for 10 min. The unreacted AgCl was filtered off, and the product was precipitated with Et_2O (8 ml) and dried in vacuum. White powder. Yield: 85 mg (54%). FT-IR (KBr, cm^{-1}): 386 (W), 399 (VW), 420 (M), 503 S, 521 (S), 619 (W), 692 (VS), 745 (S), 847 (W), 997 (M), 1011 (S), 1028 (W), 1043 (M), 1070 (W), 1096 (M), 1153 (M), 1180 (W), 1285 (M), 1312 (W), 1329 (W), 1385 (S), 1435 (S), 1479 (M), 1670 (W), 1890 (W), 1960 (W), 2853 (W), 2924 (W), 3053 (W).

*Synthesis of [Au(**1**)Cl]* Compound Au(tht)Cl (tht = tetrahydrothiophene) (65 mg, 0.20 mmol) was added to a solution of **1** (54 mg, 0.20 mmol) in CH_2Cl_2 (2 mL), and the mixture was stirred for 1 min to give a clear solution. The solvent was then evaporated, and the residue was washed with Et_2O (2 x 2 mL) and dried in vacuum. White crystalline powder. Yield: 80 mg (81 %). ^{1}H NMR (500.13 MHz, $CDCl_3$, 23 °C) δ 9.10 (H-3 in Pyr, t, J = 1.95 Hz, 1H), 8.75 (H-6 in Pyr, m, 1H), 8.68 (H-5 in Pyr, m, 1H), 7.71-7.67 (o-Ph, m, 4H), 7.57-7.55 (m-, p-Ph, m, 2H), 7.51-7.47 (m-, p-Ph, m, 4H), 7.26 ($CHCl_3$). $^{31}P\{^{1}H\}$ NMR δ (202.47 MHz, $CDCl_3$, 23 °C) 26.97. FT-IR (KBr, cm^{-1}): 392 (W), 434 (M), 515 (VS), 548 (VS), 619 (M), 689 (VS), 698 (S), 745 (S), 853 (M), 999 (M), 1011 (S), 1026 (W), 1042 (M), 1072 (W), 1101 (S), 1138 (W), 1157 (M), 1177 (W), 1281 (W) 1314 (W), 1331 (W), 1389 (M), 1435 (VS), 1479 (M), 3019 (W), 3055 (W), 3075 (W).

*Synthesis of cis-[Pt(**1**)$_2$$Cl_2$]·$CH_2Cl_2$* Compound Pt(COD)$Cl_2$ (COD = cycloocta-1,5-diene) (84 mg, 0.22 mmol) and **1** (116 mg, 0.44 mmol) were dissolved in CH_2Cl_2 (3 ml) upon stirring for 1 min. The solution volume was then reduced to 1 ml and precipitated with Et_2O (2 x 2 ml) followed by drying in vacuum to obtain the title complex. White powder. Yield: 155 mg (89%). ^{1}H NMR (500.13 MHz, $CDCl_3$, 23 °C) δ 9.01 (H-3 in Pyr, s, 1H), 8.49 (H-6 in Pyr, m, 1H), 8.43 (H-5 in Pyr, s, 1H), 7.67 (o-Ph, m, 4H), 7.38 (m-, p-Ph, m, 2H), 7.26 ($CHCl_3$), 7.21 (m-, p-Ph, m, 4H). $^{31}P\{^{1}H\}$ NMR δ (202.47 MHz, $CDCl_3$, 23 °C) 6.79 (t, J = 1835 Hz). FT-IR (KBr, cm^{-1}): 417 (W), 426 (W), 446 (M), 463 (M), 494 (S), 521 (S), 527 (S), 534 (VS), 555 (M), 619 (M), 691 (S), 731 (S), 745 (S), 847 (W), 999 (M), 1013 (S), 1043 (M), 1096 (S), 1101 (S), 1132 (M), 1148 (M), 1184 (W), 1279 (M), 1312 (W), 1389 (M), 1437 (S), 1449 (M), 1481 (M), 1557 (W), 1572 (W), 1587 (W), 2853 (W), 2926 (W), 2968 (W), 3036 (W), 3055 (W).

§3. X-Ray crystallography

The data for crystals of **1** as well as [Au(**1**)Cl], *cis*-[Pt(**1**)$_2$Cl$_2$]·CH$_2$Cl$_2$, and [Ag$_4$Cl$_4$(**1**)$_4$] were collected 296 K on a Bruker Kappa Apex II CCD diffractometer using φ,ω-scans of narrow (0.5°) frames with MoKα radiation (λ = 0.71073 Å) and a graphite monochromator. The structures were solved by dual space algorithm (SHELXT) and refined by the full-matrix least squares technique (SHELXL) in the anisotropic approximation (except hydrogen atoms). Positions of hydrogen atoms of organic ligands were calculated geometrically and refined in the riding model.

Single crystals of **1** were obtained by slow cooling of its saturated MeOH solution. Single crystals of [Au(**1**)Cl], *cis*-[Pt(**1**)$_2$Cl$_2$]·CH$_2$Cl$_2$, [Ag$_4$Cl$_4$(**1**)$_4$] were obtained by slow vapor diffusion of Et$_2$O into saturated CH$_2$Cl$_2$, MeOH and DMF solution of complexes [Au(**1**)Cl], *cis*-[Pt(**1**)$_2$Cl$_2$] and [Ag$_4$Cl$_4$(**1**)$_4$], respectively.

Table S1. Selected bond lengths (Å) and angles (˚) for compounds **1**, [Au(**1**)Cl], *cis*-[Pt(**1**)$_2$Cl$_2$]·CH$_2$Cl$_2$ and [Ag$_4$Cl$_4$(**1**)$_4$].

1			
P1–C4	1.8298(15)	P1–C3	1.8458(15)
P1–C11	1.8328(15)	C4–P1–C11	105.06(6)
C11–P1–C3	99.60(6)	C4–P1–C3	100.38(7)
[Au(**1**)Cl]			
Au1–P1	2.225(4)	Au1–Cl1	2.276(4)
P1–Au1–Cl1	178.3(7)		
cis-[Pt(**1**)$_2$Cl$_2$]·CH$_2$Cl$_2$			
Pt1–P1	2.2463(11)	Pt1–Cl2	2.3408(12)
Pt1–P2	2.2490(11)	Pt1–Cl1	2.3504(14)
P1–Pt1–P2	100.21(4)	P1–Pt1–Cl1	171.16(5)
P1–Pt1–Cl2	86.86(4)	P2–Pt1–Cl1	85.01(5)
P2–Pt1–Cl2	172.12(4)	Cl2–Pt1–Cl1	88.43(5)
[Ag$_4$Cl$_4$(**1**)$_4$]			
Ag1–P4	2.4023(13)	Ag3–P1	2.3897(11)
Ag1–Cl3	2.5947(13)	Ag3–Cl3	2.5955(12)
Ag1–Cl4	2.7050(14)	Ag3–Cl2	2.6825(11)
Ag1–Cl1	2.7186(13)	Ag3–Cl1	2.6962(12)
Ag2–P3	2.3816(12)	Ag4–P2	2.3979(11)
Ag2–Cl1	2.5285(11)	Ag4–Cl2	2.5763(11)
Ag2–Cl2	2.7182(11)	Ag4–Cl4	2.6517(13)
Ag2–Cl4	2.7491(13)	Ag4–Cl3	2.8100(12)
P4–Ag1–Cl3	128.92(5)	P2–Ag4–Cl2	133.77(4)
P4–Ag1–Cl4	116.61(5)	P2–Ag4–Cl4	122.73(4)
Cl3–Ag1–Cl4	93.69(4)	Cl2–Ag4–Cl4	93.43(4)
P4–Ag1–Cl1	122.29(5)	P2–Ag4–Cl3	115.35(4)
Cl3–Ag1–Cl1	93.30(4)	Cl2–Ag4–Cl3	89.73(3)
Cl4–Ag1–Cl1	93.55(4)	Cl4–Ag4–Cl3	90.10(4)
P3–Ag2–Cl1	136.92(4)	Ag2–Cl1–Ag3	92.34(3)
P3–Ag2–Cl2	118.92(4)	Ag2–Cl1–Ag1	86.77(4)
Cl1–Ag2–Cl2	90.77(4)	Ag3–Cl1–Ag1	84.16(3)
P3–Ag2–Cl4	113.30(4)	Ag4–Cl2–Ag3	90.62(3)
Cl1–Ag2–Cl4	96.89(4)	Ag4–Cl2–Ag2	90.24(3)
Cl2–Ag2–Cl4	88.24(3)	Ag3–Cl2–Ag2	88.56(3)
P1–Ag3–Cl3	125.31(4)	Ag1–Cl3–Ag3	88.72(4)
P1–Ag3–Cl2	121.80(4)	Ag1–Cl3–Ag4	87.34(4)
Cl3–Ag3–Cl2	92.19(3)	Ag3–Cl3–Ag4	87.45(3)
P1–Ag3–Cl1	125.51(4)	Ag4–Cl4–Ag1	88.41(4)
Cl3–Ag3–Cl1	93.80(4)	Ag4–Cl4–Ag2	88.02(4)
Cl2–Ag3–Cl1	88.02(3)	Ag1–Cl4–Ag2	82.79(4)

§4. NMR spectra

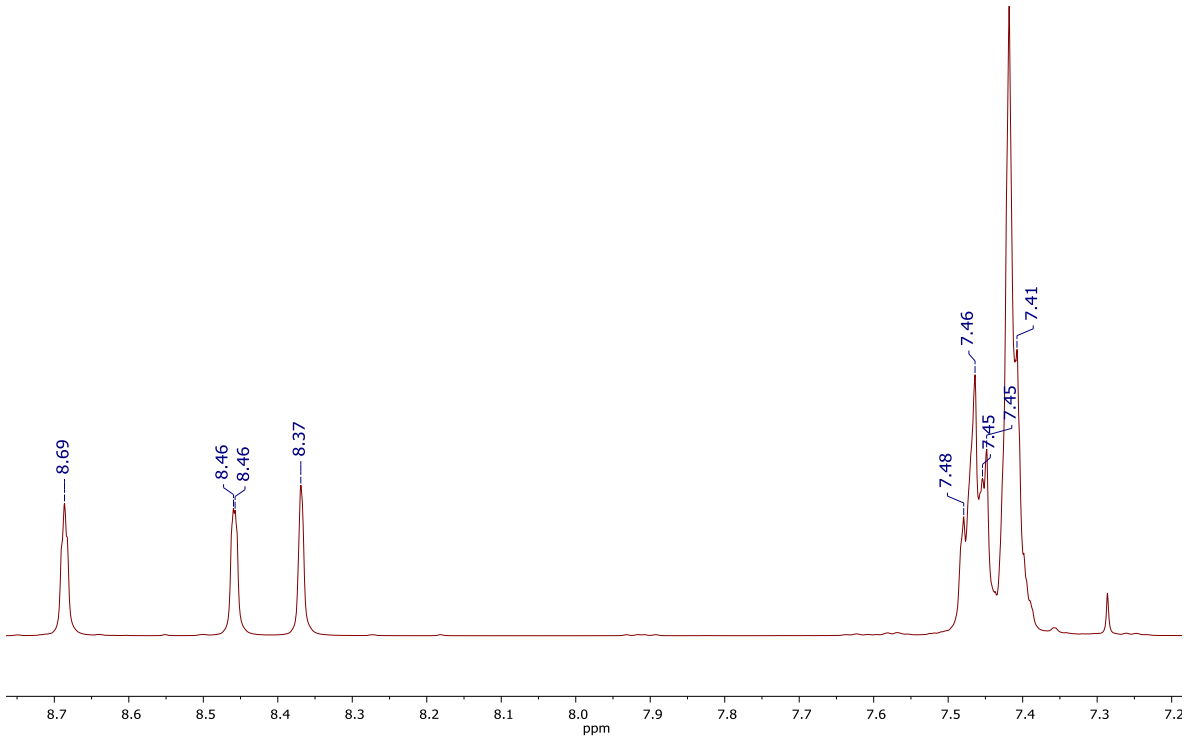

Figure S1. ^{1}H NMR spectrum of **1** ($CDCl_3$, 23 °C).

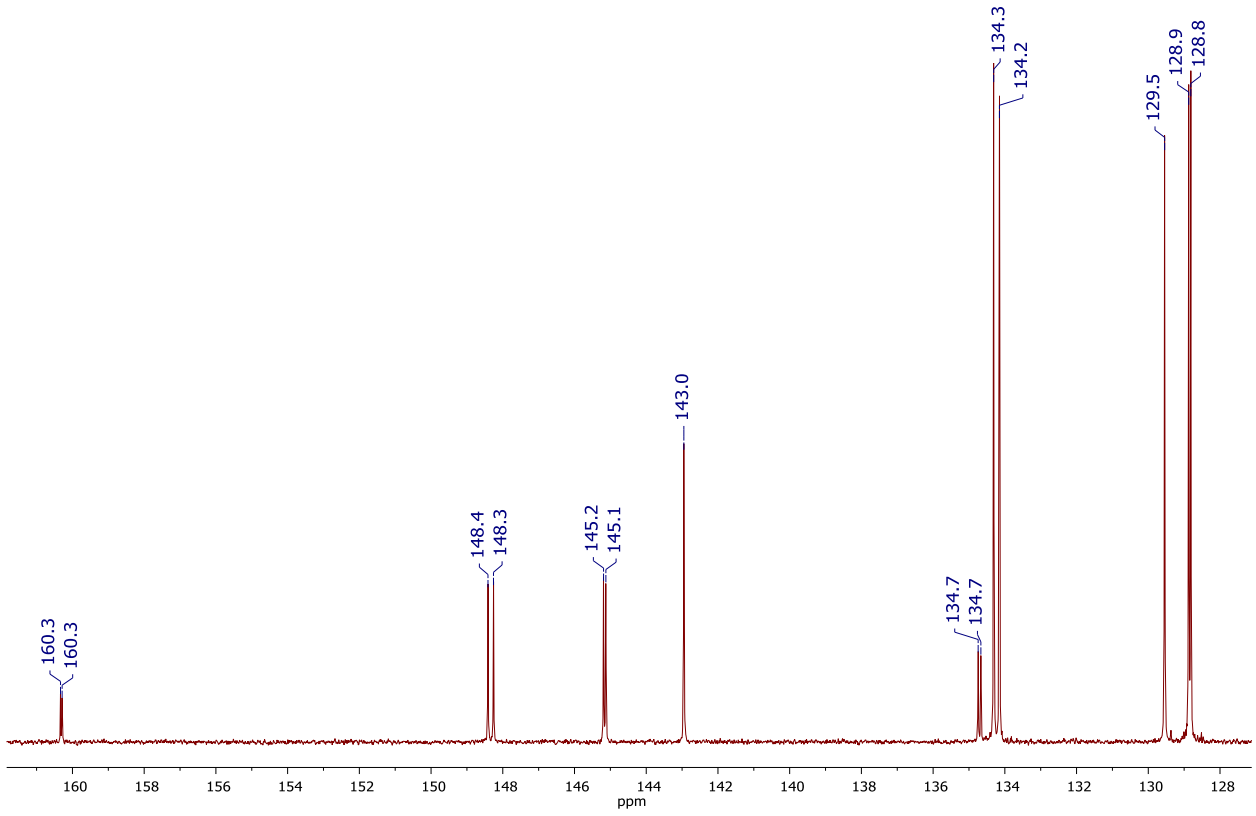

Figure S2. $^{13}C\{^{1}H\}$ NMR spectrum of **1** (CH_2Cl_2, 23 °C).

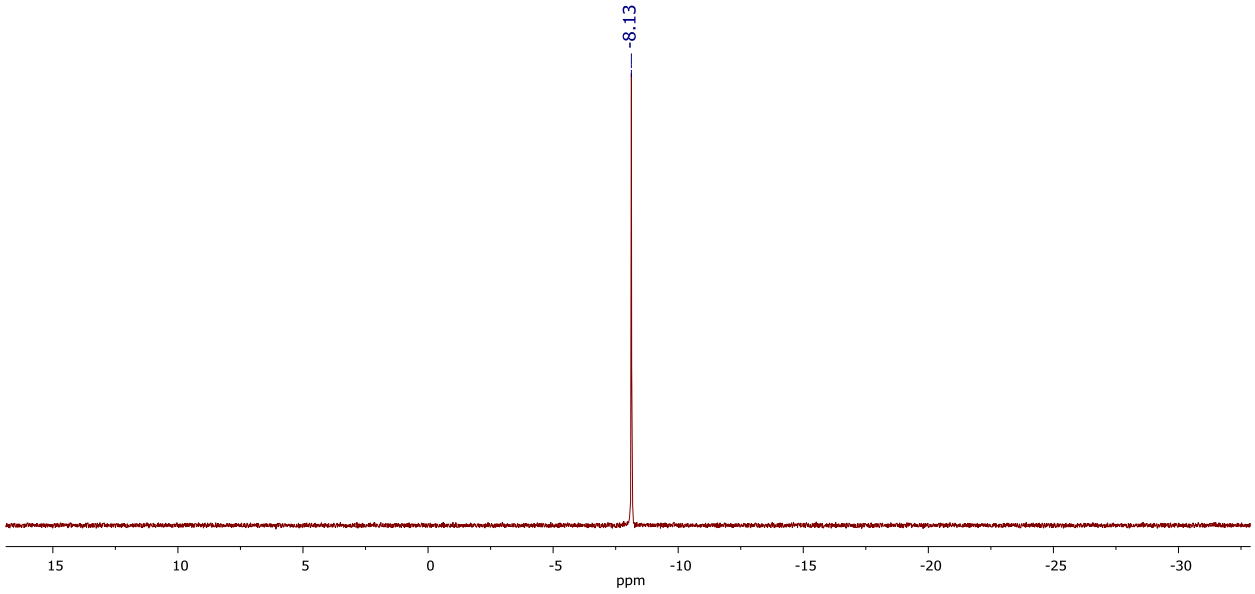

Figure S3. $^{31}P\{^{1}H\}$ NMR spectrum of **1** (CH_2Cl_2, 23 °C).

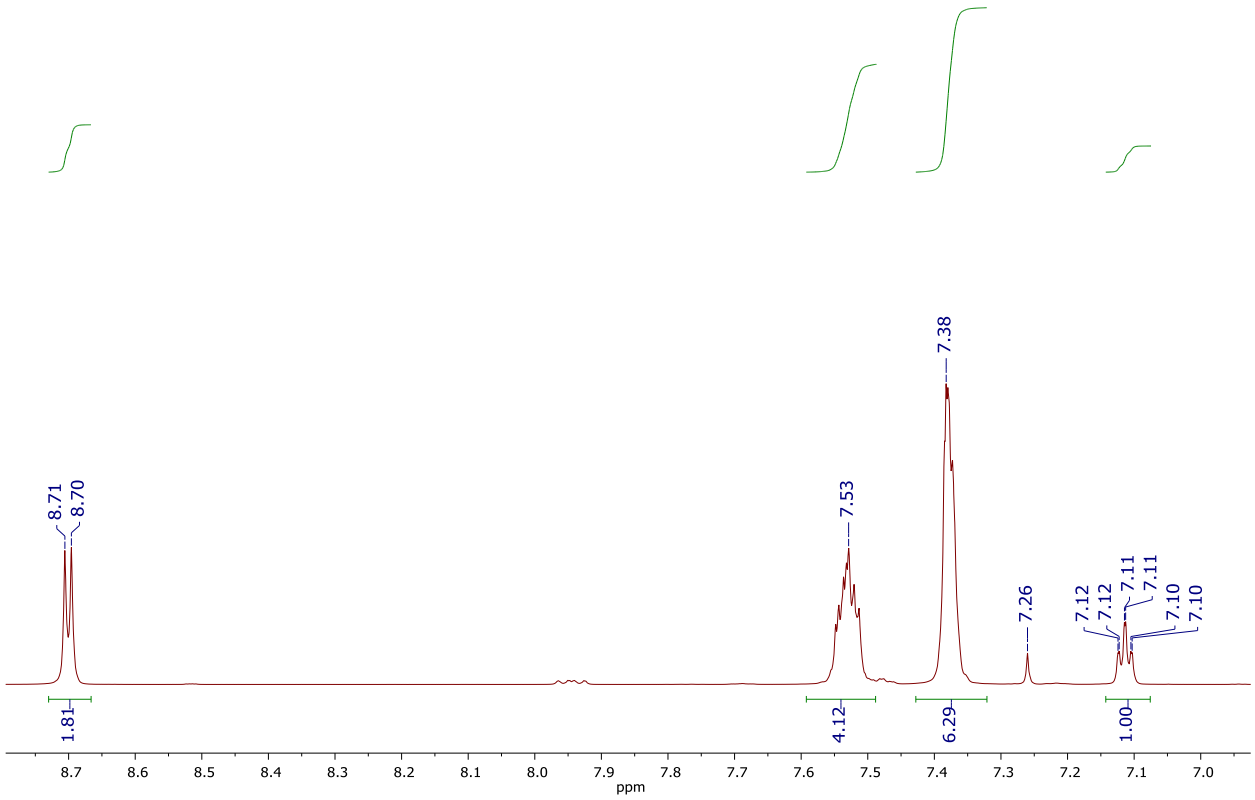

Figure S4. ^{1}H NMR spectrum of **2** ($CDCl_3$, 23 °C).

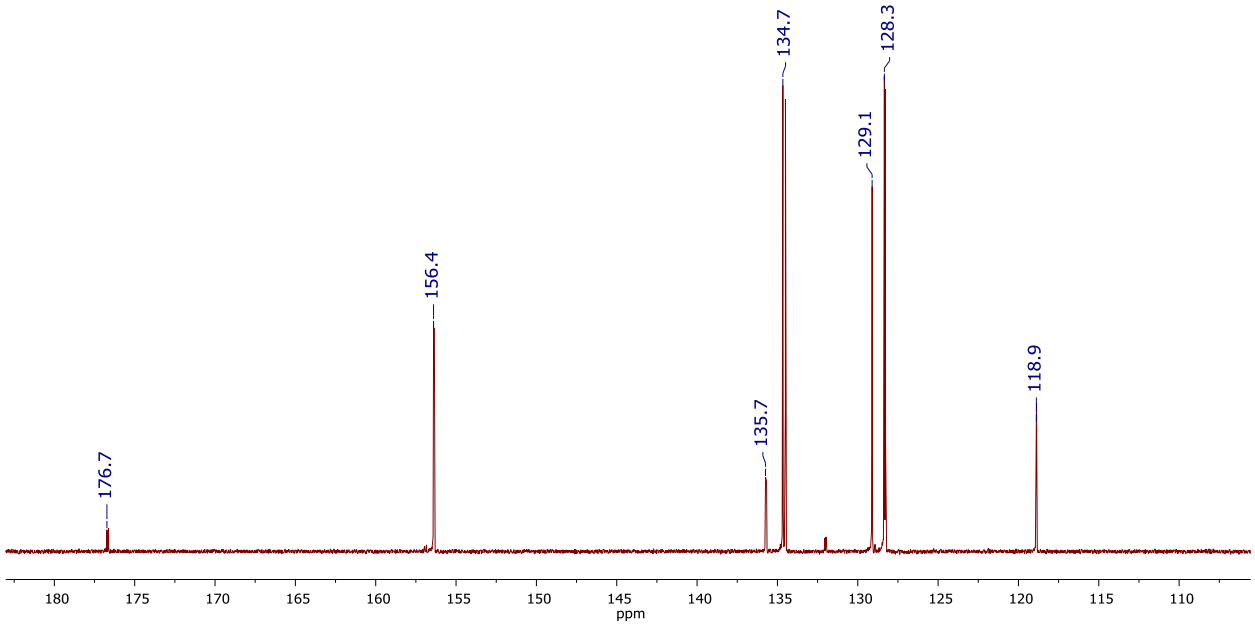

Figure S5. $^{13}C\{^{1}H\}$ NMR spectrum of **2** (CH_2Cl_2, 23 °C).

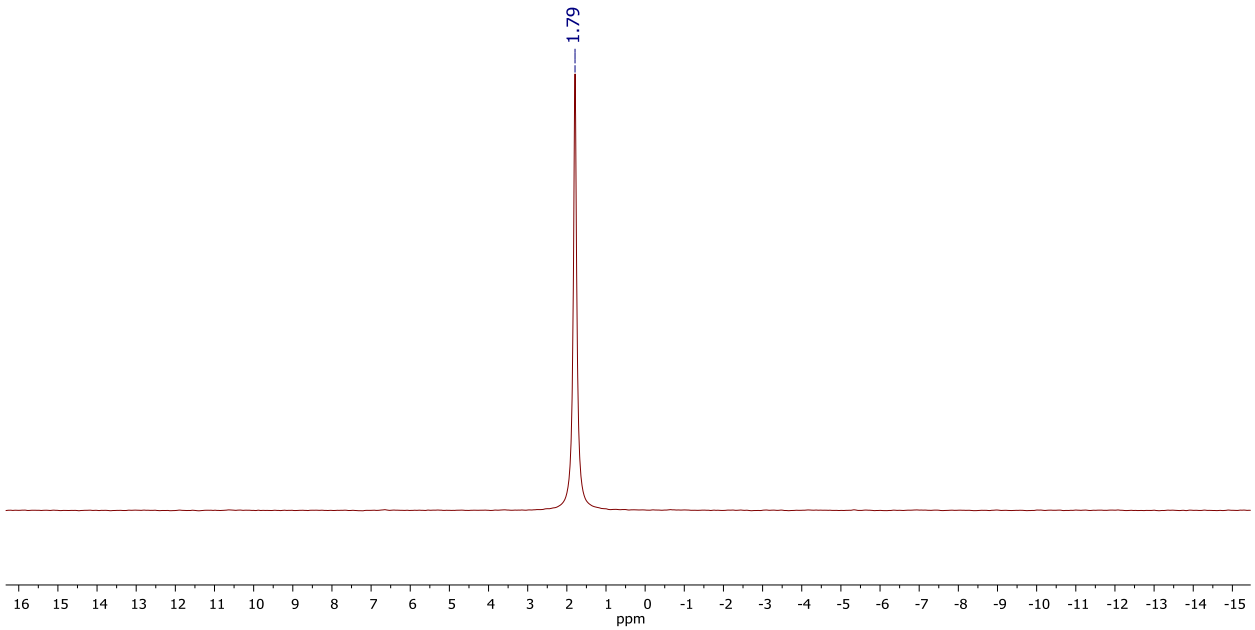

Figure S6. $^{31}P\{^{1}H\}$ NMR spectrum of **2** (CH_2Cl_2, 23 °C).

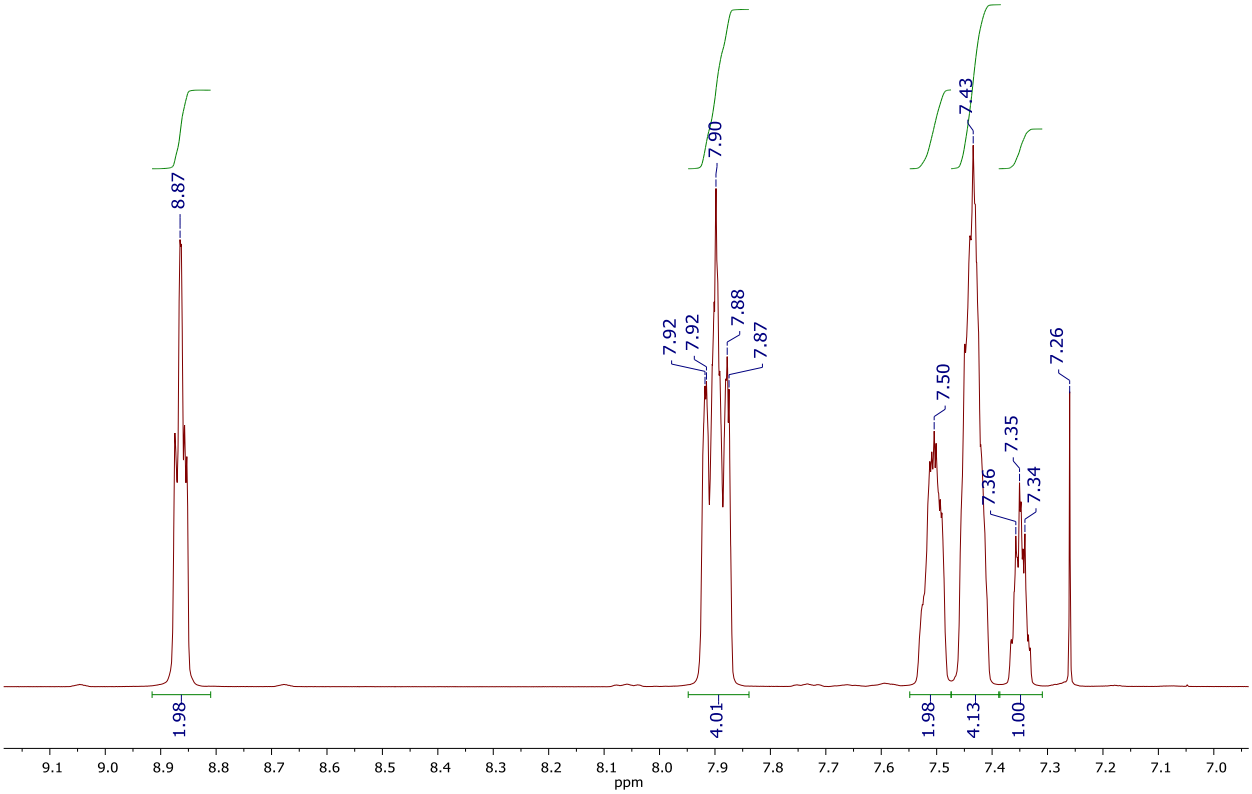

Figure S7. ^{1}H NMR spectrum of **3** ($CDCl_3$, 23 °C).

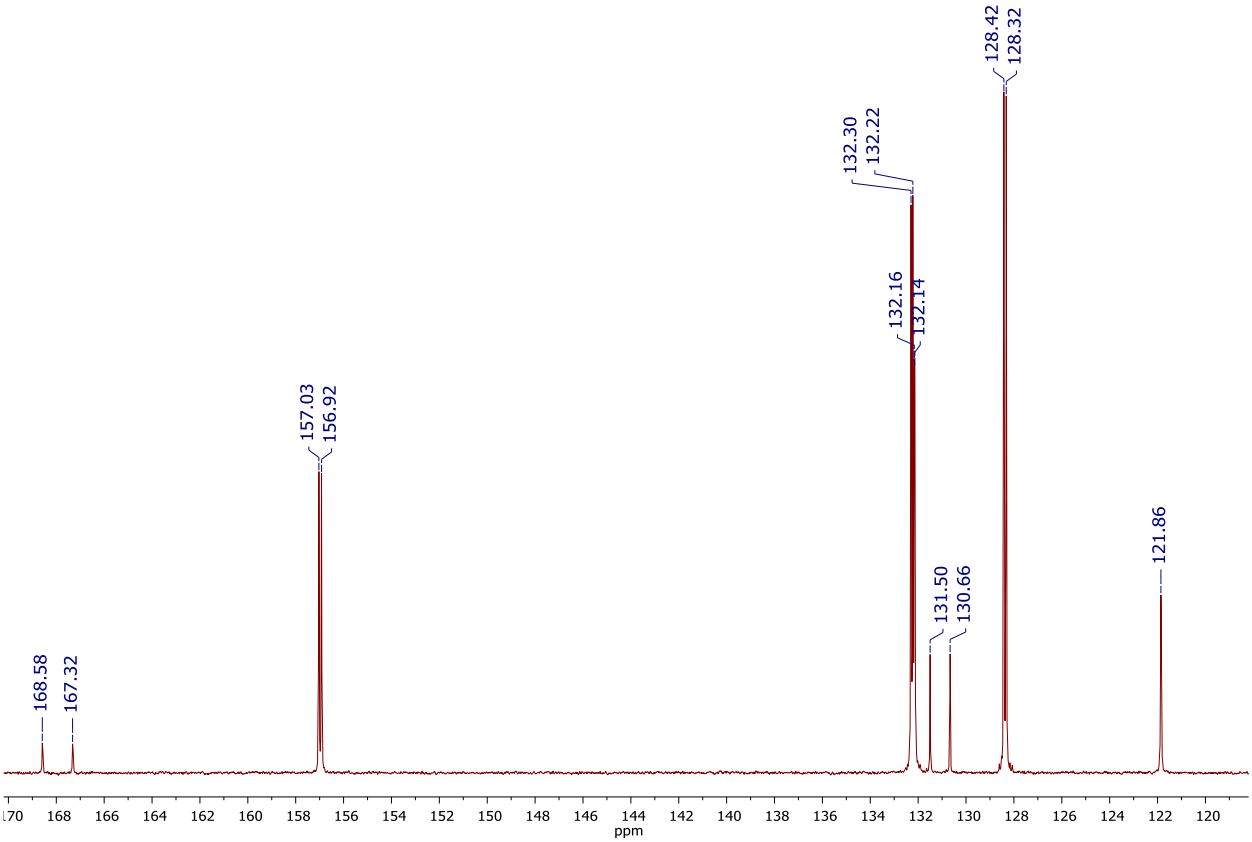

Figure S8. $^{13}C\{^{1}H\}$ NMR spectrum of **3** (CH_2Cl_2, 23 °C).

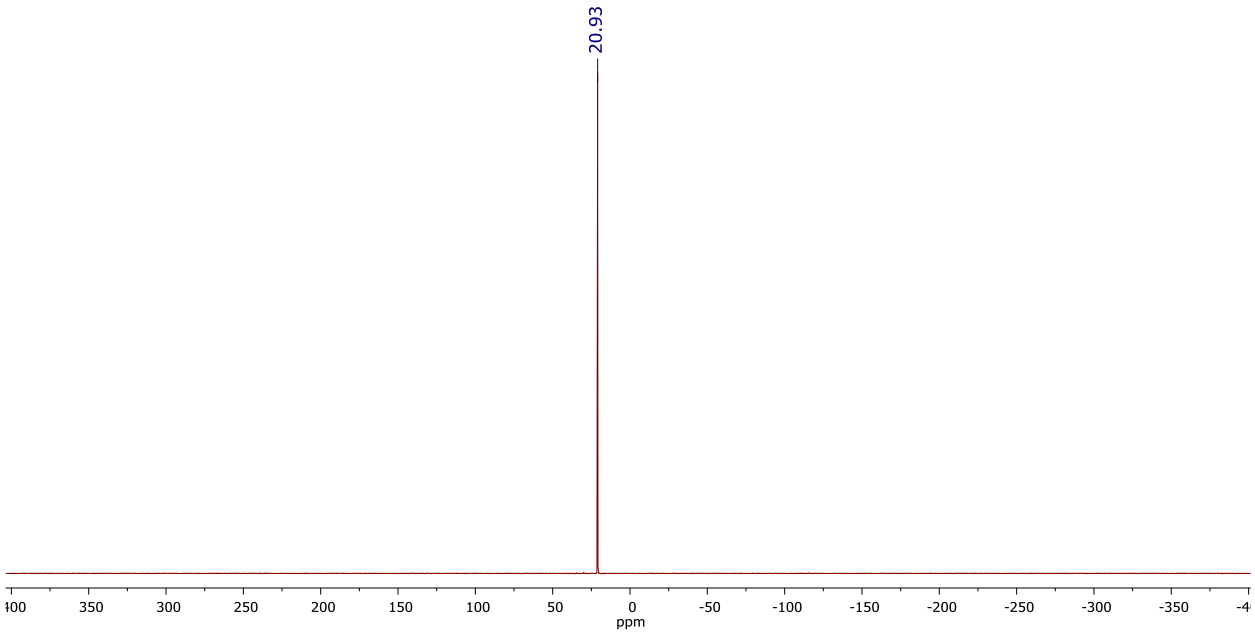

Figure S9. $^{31}P\{^{1}H\}$ NMR spectrum of **3** (CH_2Cl_2, 23 °C).

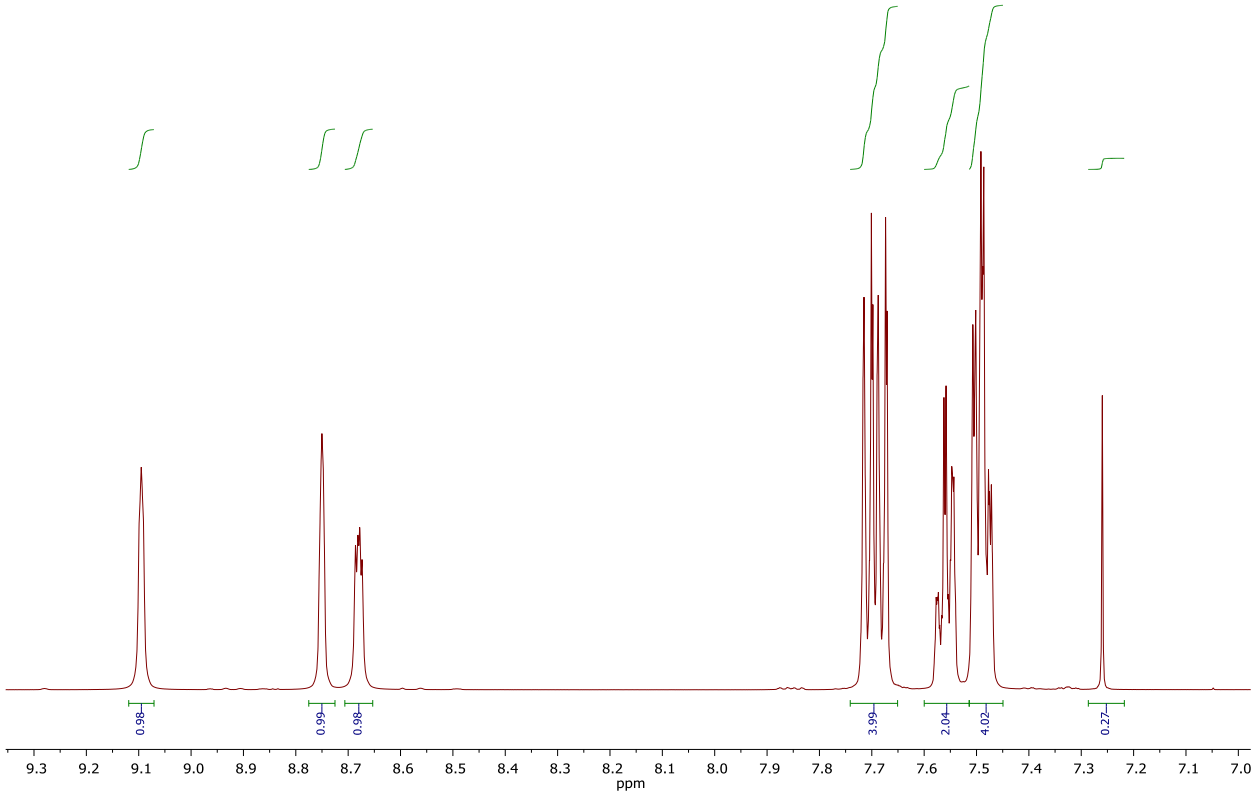

Figure S10. ^{1}H NMR spectrum of [Au(**1**)Cl] ($CDCl_3$, 23 °C).

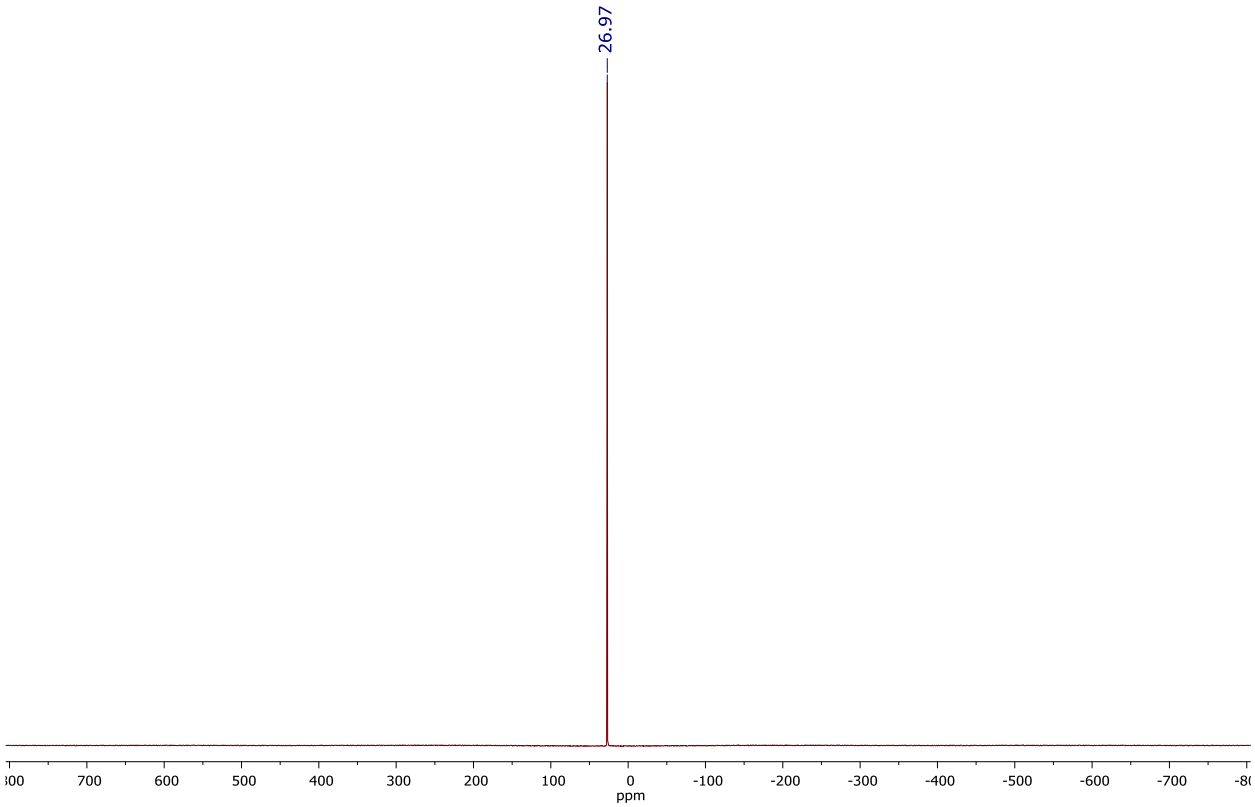

Figure S11. $^{31}P\{^{1}H\}$ NMR spectrum of [Au(**1**)Cl] ($CDCl_3$, 23 °C).

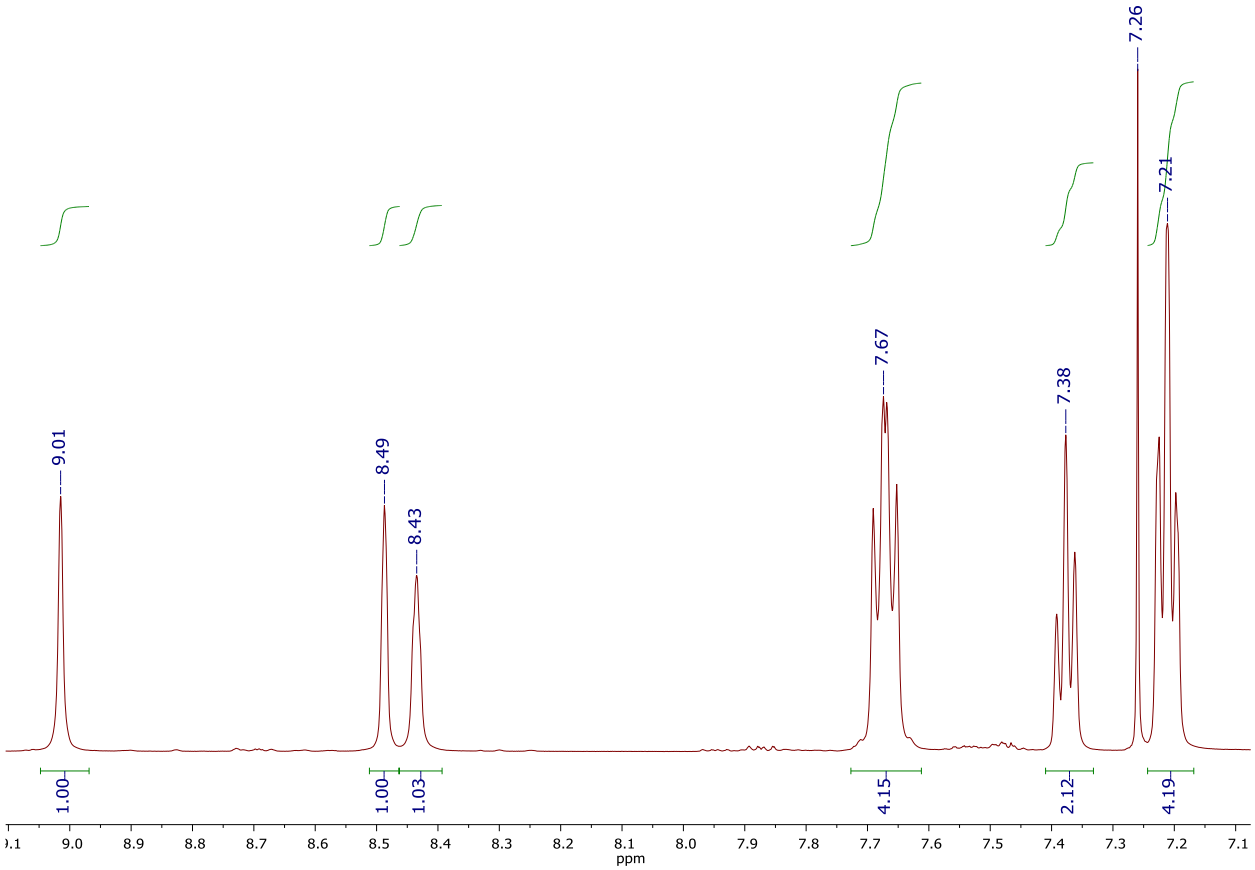

Figure S12. ^{1}H NMR spectrum of *cis*-[Pt(**1**)$_2$Cl$_2$] ($CDCl_3$, 23 °C).

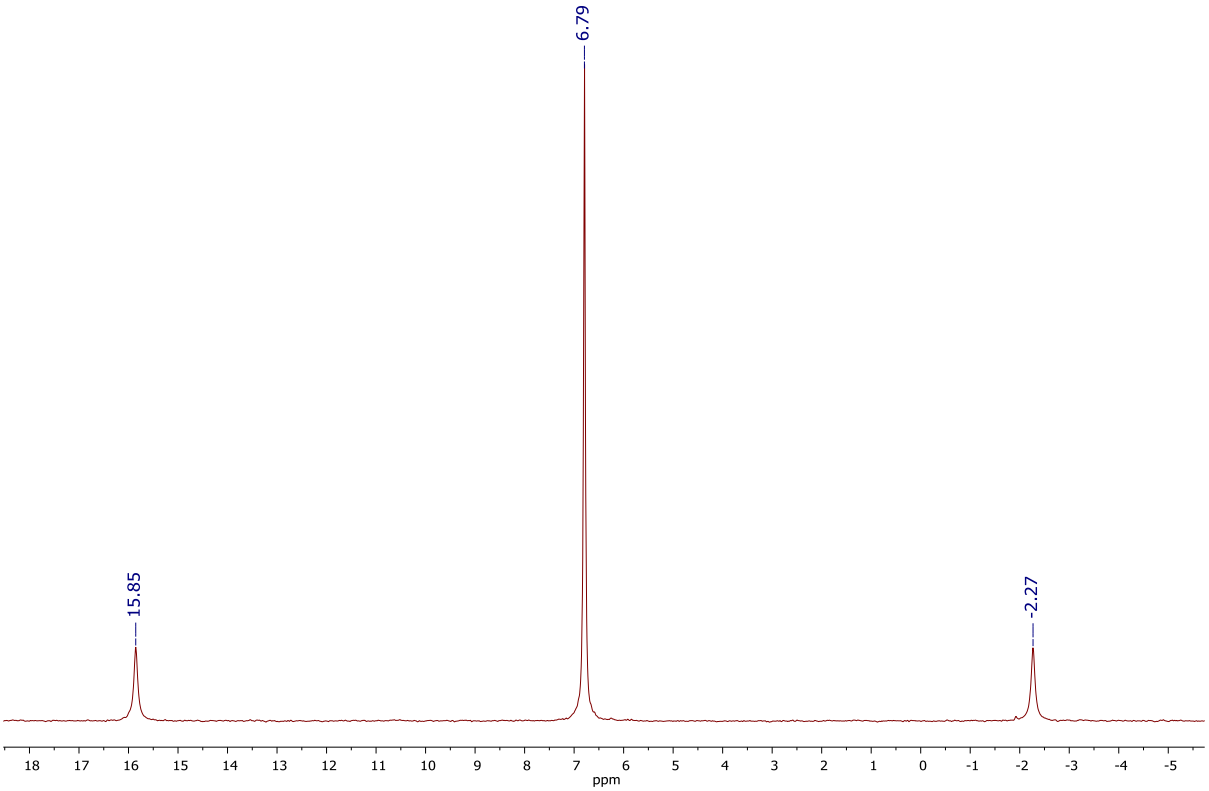

Figure S13. $^{31}P\{^{1}H\}$ NMR spectrum of *cis*-[Pt(**1**)$_2$Cl$_2$] ($CDCl_3$, 23 °C).

§5. Thermogravimetric analysis

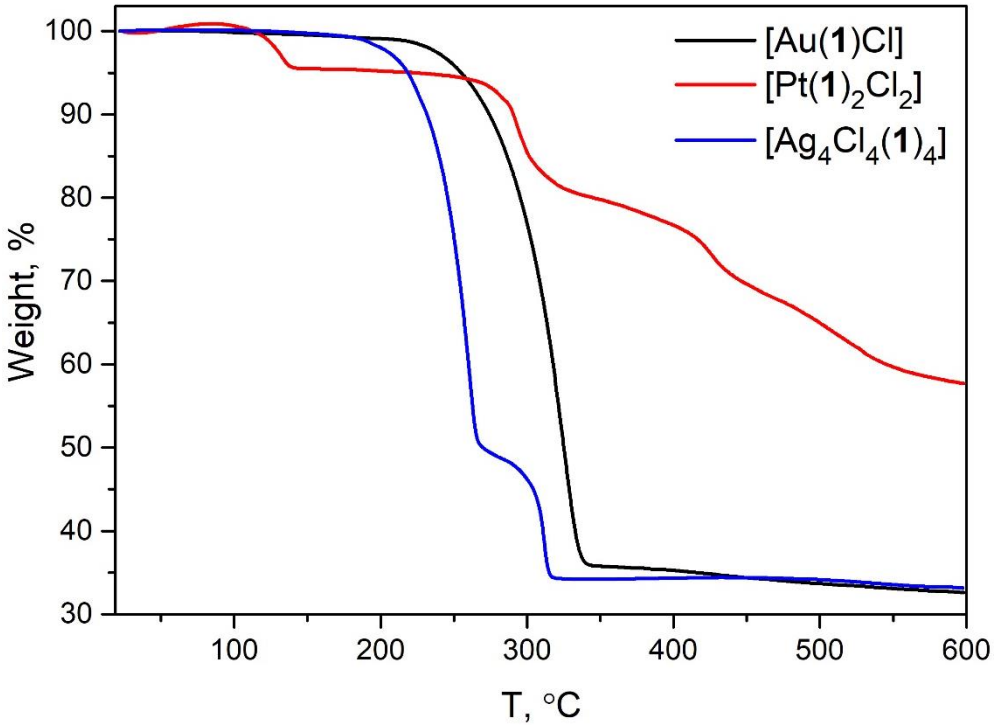

Figure S14. TG curves of complexes [Au(**1**)Cl], *cis*-[Pt(**1**)$_2$Cl$_2$]·CH$_2$Cl$_2$ and [Ag$_4$Cl$_4$(**1**)$_4$].

§6. FT-IR spectra

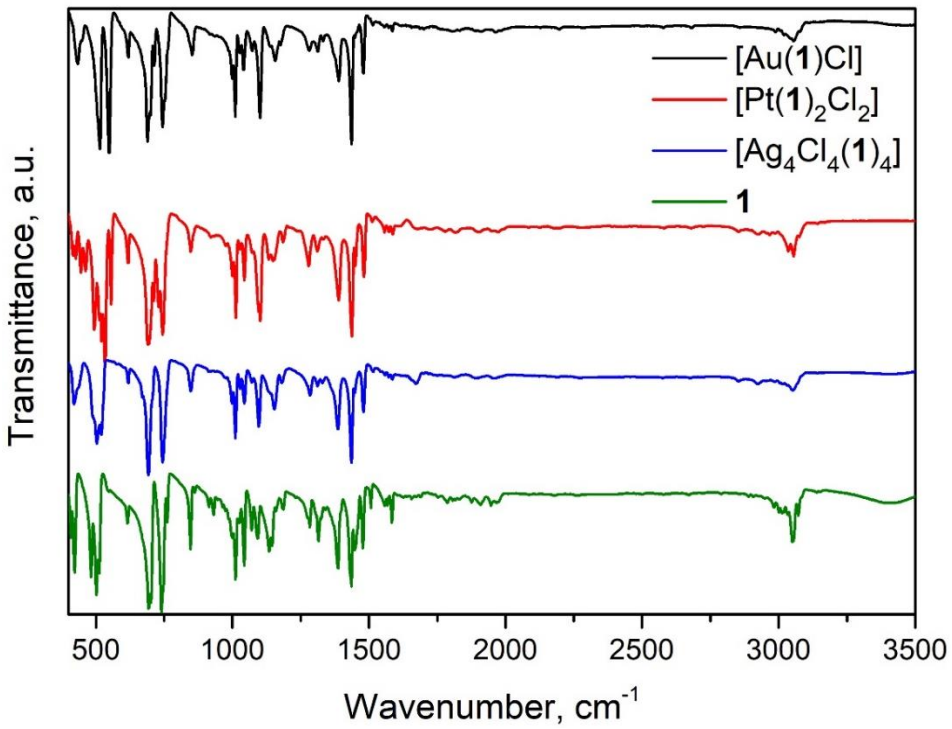

Figure S15. FT-IR spectra of phosphine **1** as well as [Au(**1**)Cl], *cis*-[Pt(**1**)$_2$Cl$_2$]·CH$_2$Cl$_2$, and [Ag$_4$(**1**)$_4$Cl$_4$].