Supporting information for:

Digold Phosphinine Complexes Are Stable with a Bis(Phosphinine) Ligand but Not with a 2-Phosphinophosphinine

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Contents

[(AuCl)$_2$[bis{3-methyl-6-(trimethylsilyl)phosphinine-2-yl}dimethylsilane]] (21)
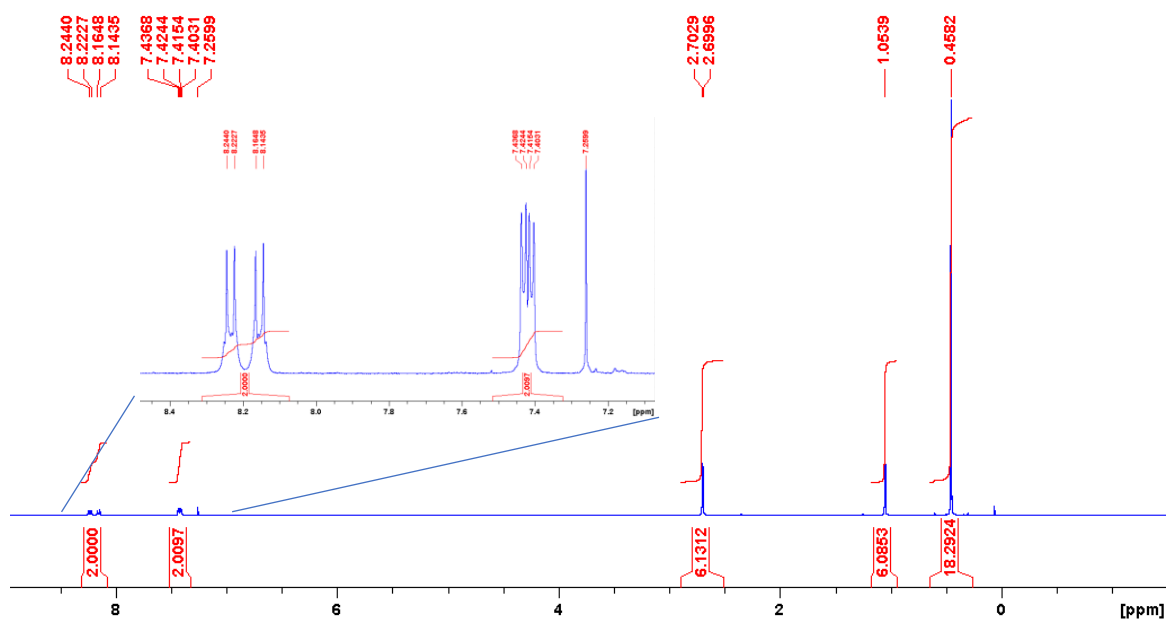
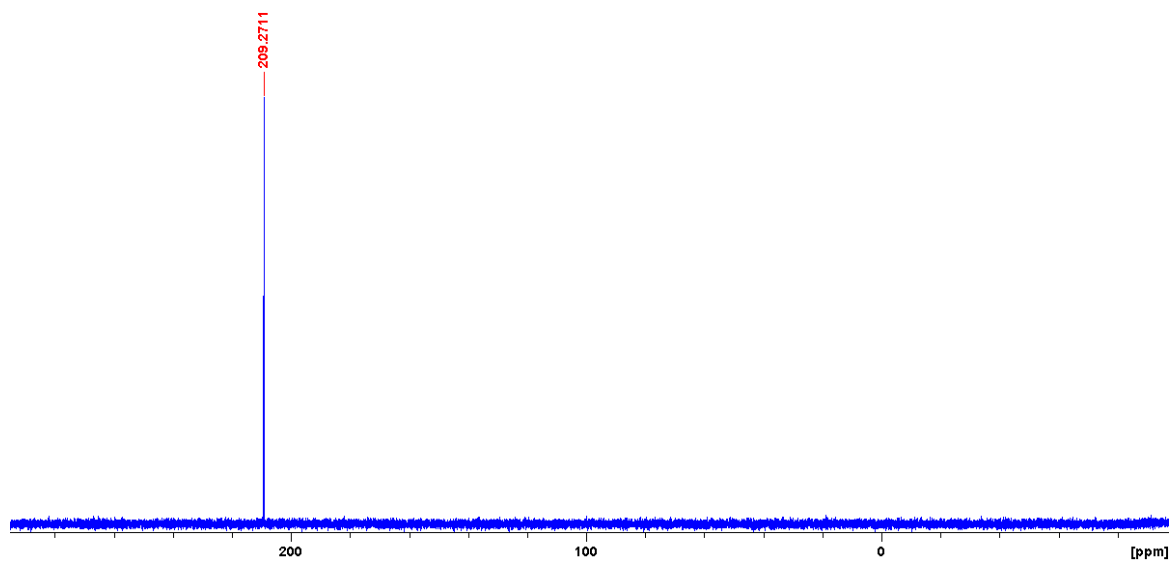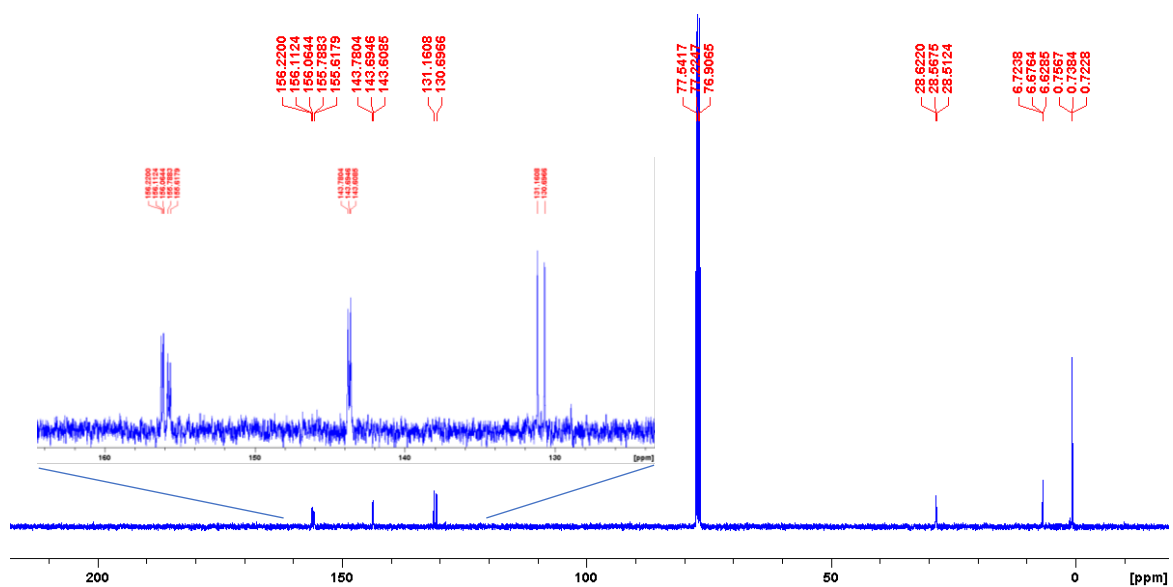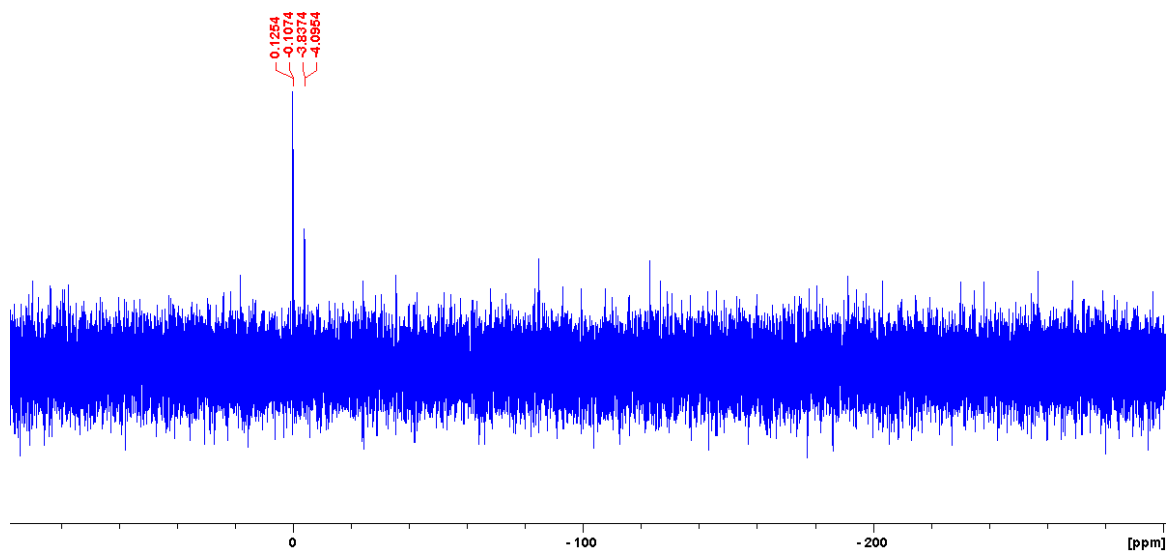**Figure S1.** ^{1}H NMR (400 MHz, CDCl$_3$, 298 K) spectrum of **21**.

Figure S2. $^{31}P\{^{1}H\}$ NMR (162 MHz, CDCl$_3$, 298 K) spectrum of **21**.

Figure S3. $^{13}C\{^{1}H\}$ NMR (100.6 MHz, CDCl$_3$, 298 K) spectrum of **21**.
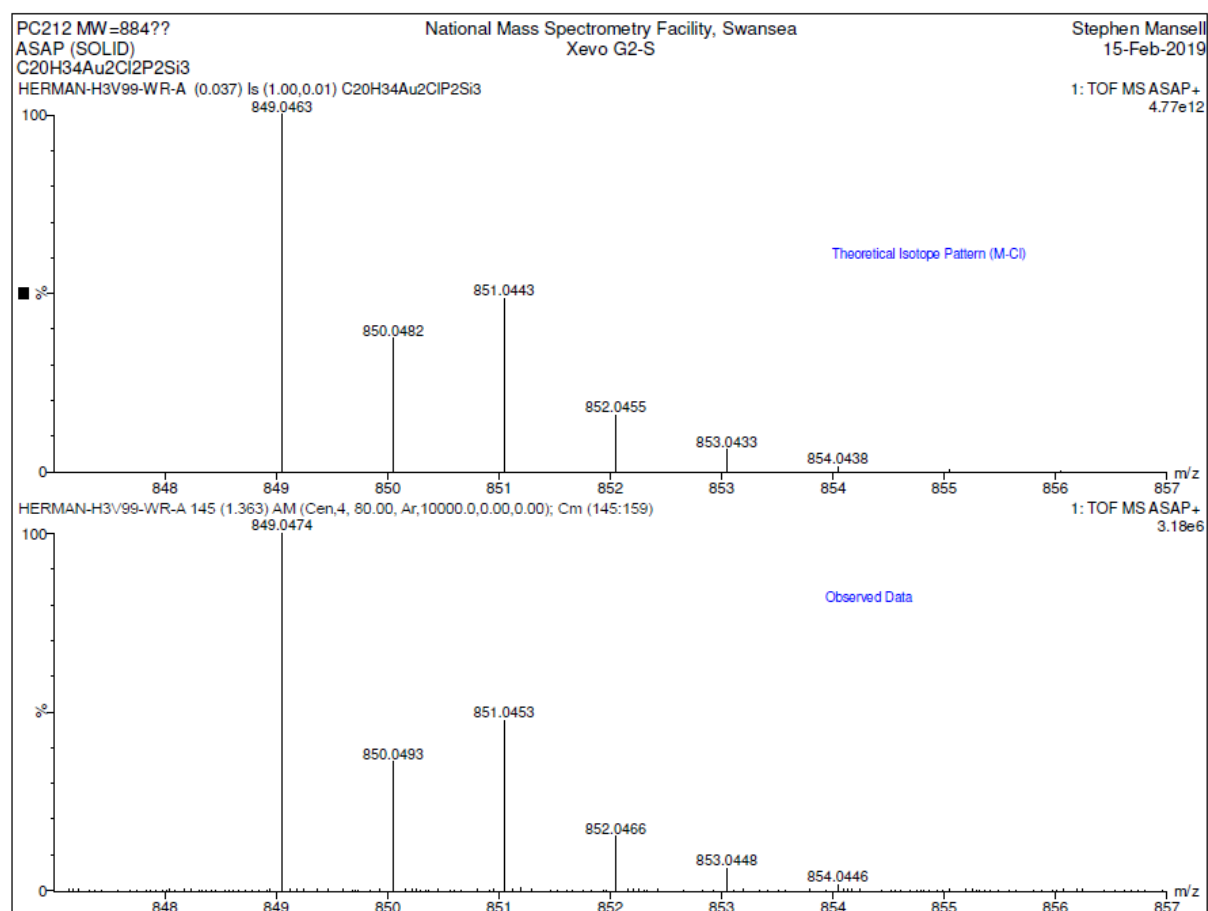
Figure S4. $^{29}Si\{^1H\}$ NMR (79.5 MHz, $CDCl_3$, 298 K) spectrum of **21**.
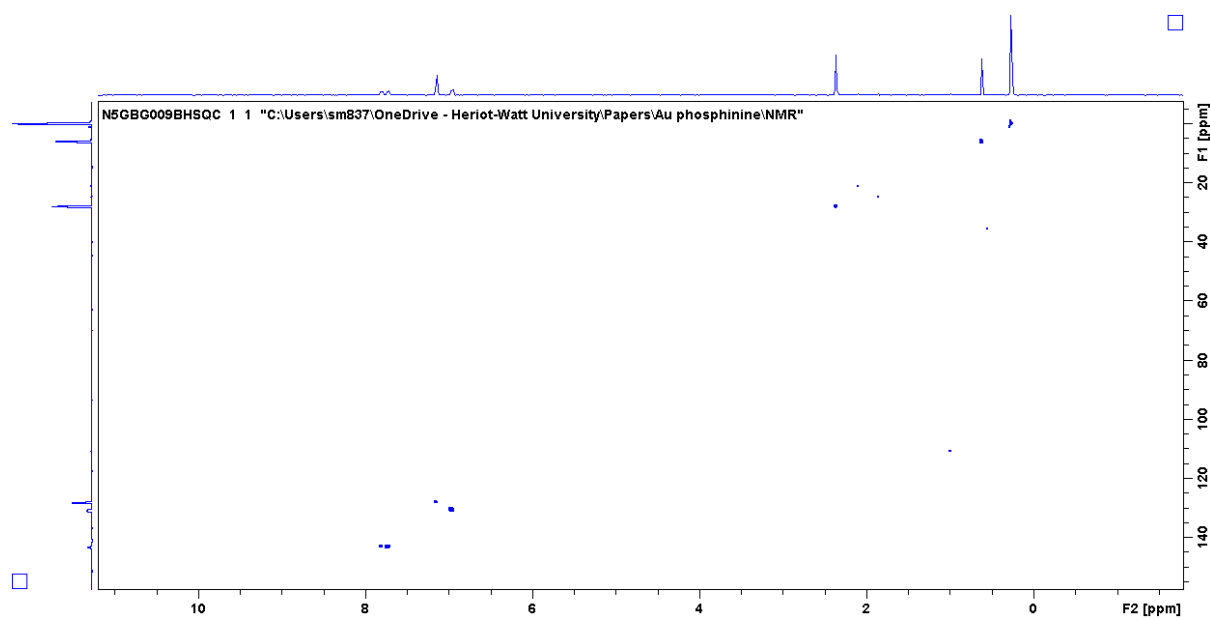
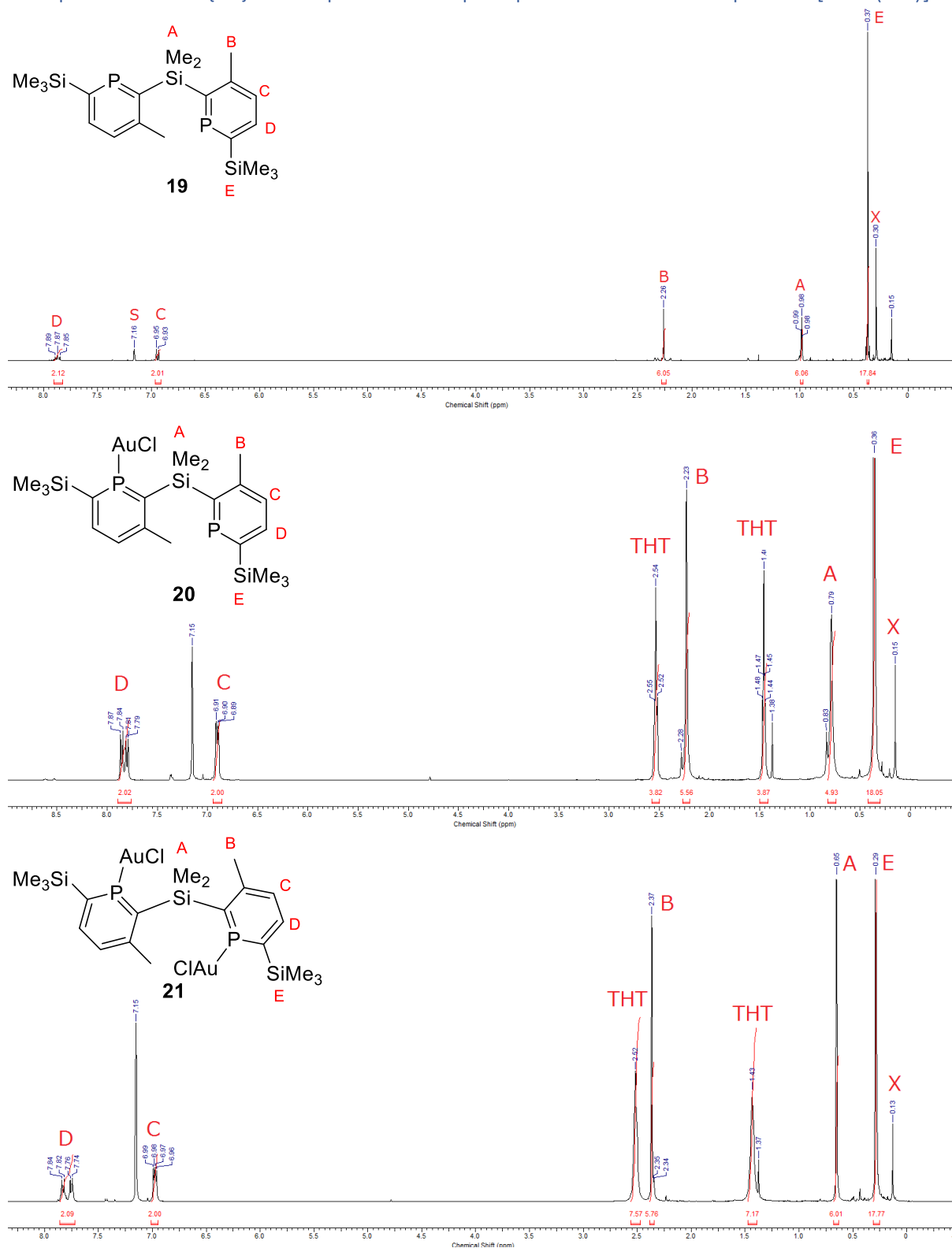**Figure S5.** HSQC spectrum (C_6D_6) used to assign *para* and *meta* phosphinine C-H for **21**.
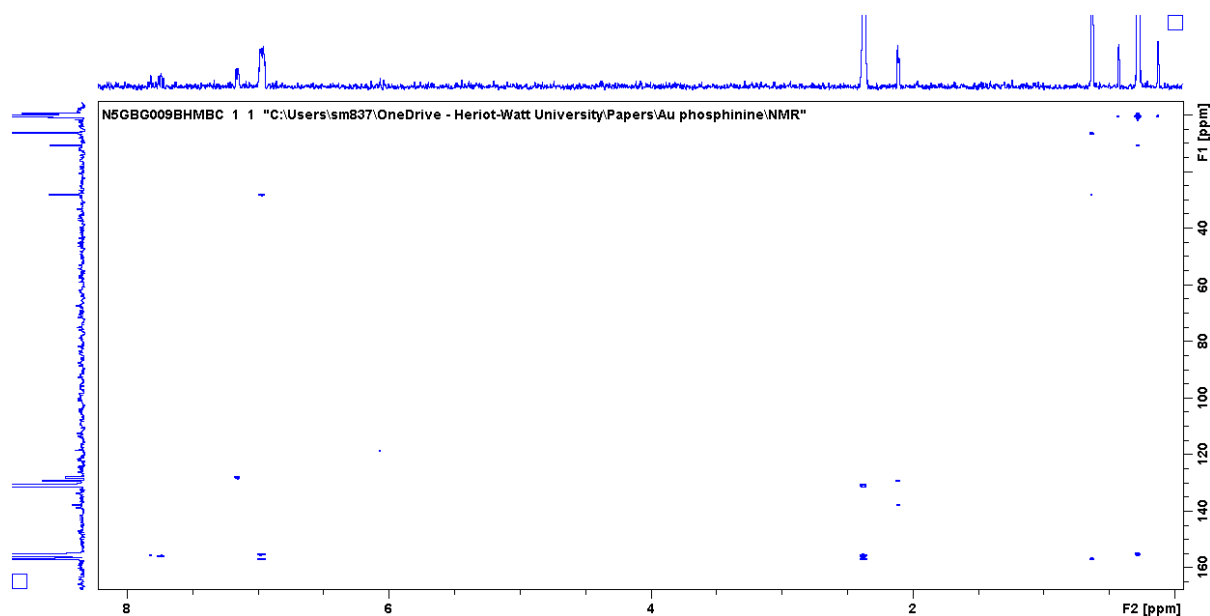
Figure S6. HMBC spectrum (C_6D_6) used to assign the two *ortho*-C in **21** from coupling to $SiMe_3$ and $SiMe_2$.

Figure S7. Accurate mass and isotope distribution for M-Cl (**21**).

Comparison of $^{31}P\{^1H\}$ NMR spectra for diphosphinine + 1 and 2 equivs of [AuCl(tht)]

Figure S8. Comparison of ^1H NMR spectra (C_6D_6) for diphosphinine **19** (top) with the products formed after addition of one (**20**, middle) and two (**21**, bottom) equivalents of [AuCl(tht)]. X = silicon grease impurity. S = residual protio solvent peak in deuterated solvent.

Variable temperature ^{31}P{^{1}H} NMR spectra of mono gold complex 20
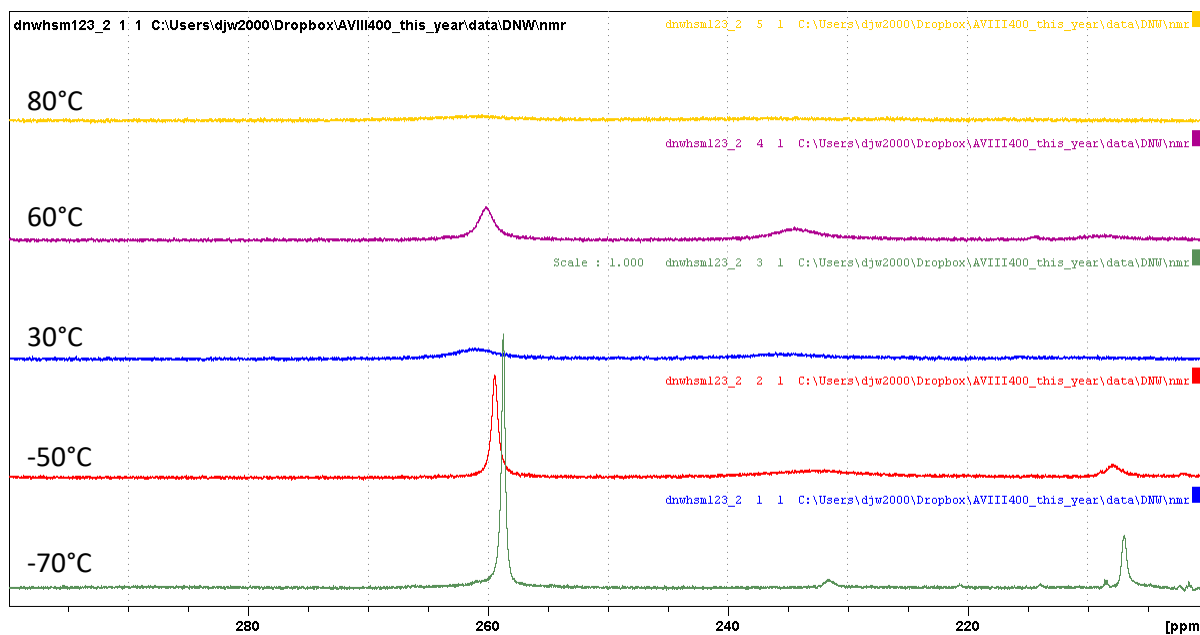
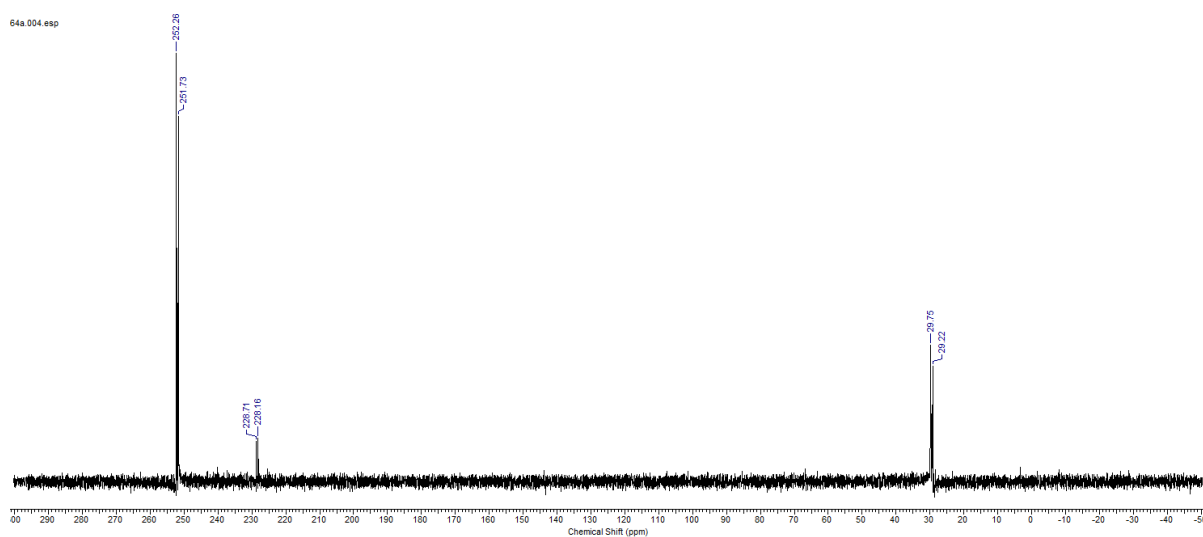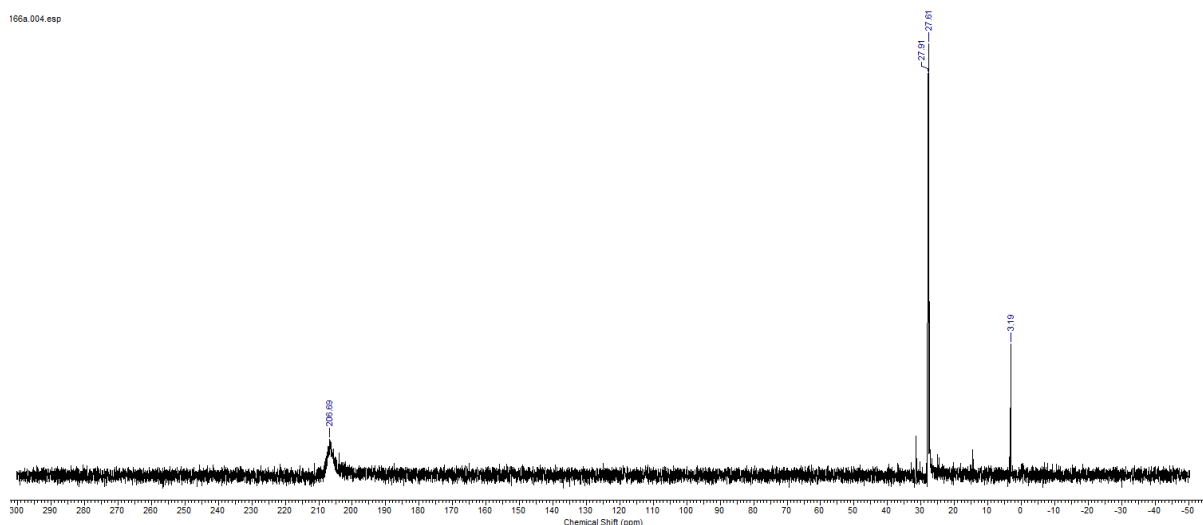**Figure S9.** Stack plot of ^{31}P{^{1}H} NMR spectra (d^8-toluene) of mono gold complex **20**. Yellow: 80°C, purple: 60°C, blue: 30°C, red: -50°C, green: -70°C.

Reaction of 1 equiv. [AuCl(tht)] with phosphinophosphinine 22.

Figure S10. ^{31}P{^{1}H} NMR (162 MHz, CDCl$_3$, 298 K) spectrum of **23**. Resonance at 226 ppm is from an unknown impurity.

Reaction of 2 equivs [AuCl(tht)] with phosphinophosphinine 22.

Figure S11. $^{31}P\{^1H\}$ NMR (162 MHz, C_6D_6, 298 K) spectrum of **24**. Resonance at 3 ppm is from an unknown impurity.

Reaction of 2 equivs [AuCl(SMe₂)] with phosphinophosphinine 22 under wet conditions.
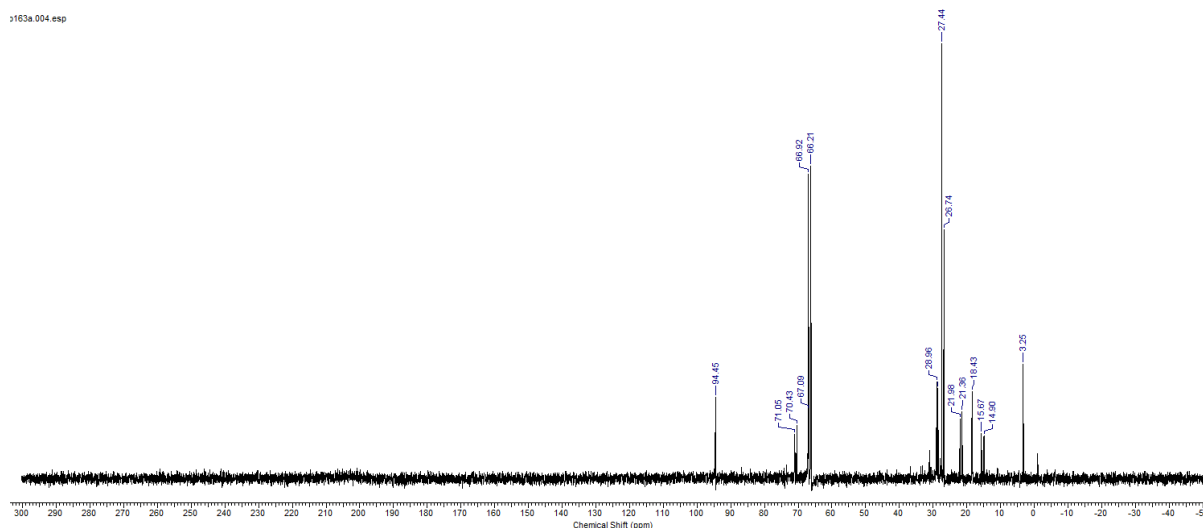
Figure S12. $^{31}P\{^1H\}$ NMR (162 MHz, C_6D_6, 298 K) spectrum of **25** + other products.

Crystallographic details

Table S1. Additional crystallographic data.

	21	25·CHCl₃
Empirical formula	$C_{20}H_{34}Au_2Cl_2P_2Si_3$	$C_{19}H_{19}Au_2Cl_5OP_2$
Formula weight	885.51	896.46
T/K	100.0	100.0
Crystal system	monoclinic	triclinic
Space group	$C2/c$	P-1
a/Å	12.4701(6)	7.9896(6)
b/Å	11.9976(8)	12.4698(9)
c/Å	20.0484(10)	12.7913(9)
α/°	90	96.440(4)
β/°	103.264(2)	98.276(3)
γ/°	90	99.158(3)
Volume/Å³	2919.4(3)	1233.08(16)
Z	4	2
ρ_{calc}g/cm³	2.015	2.414
μ/mm¹	22.576	12.566
F(000)	1672.0	828.0
Crystal size/mm³	0.32 × 0.3 × 0.12	0.4 × 0.36 × 0.34
Radiation	CuK_{α} (λ = 1.54178)	MoK_{α} (λ = 0.71073)
2Θ range for data collection/°	9.064 to 155.152	5.236 to 66.582
Index ranges	-15 ≤ h ≤ 15, -15 ≤ k ≤ 13, -25 ≤ l ≤ 25	-12 ≤ h ≤ 12, -19 ≤ k ≤ 19, -19 ≤ l ≤ 19
Reflections collected	29676	34735
Independent reflections	3074 [R_{int} = 0.0281, R_{sigma} = 0.0143]	9332 [R_{int} = 0.0477, R_{sigma} = 0.0491]
Data/ restraints/ parameters	3074/0/138	9332/0/264
Goodness-of-fit on F²	1.210	1.034
Final R indexes [I>=2σ (I)]	R_1 = 0.0322, $_wR_2$ = 0.0874	R_1 = 0.0295, wR₂ = 0.0578
Final R indexes [all data]	R_1 = 0.0322, $_wR_2$ = 0.0874	R_1 = 0.0425, wR₂ = 0.0612
Largest diff. peak/hole (e Å⁻³)	2.10/-2.47	1.36/-1.78