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Supporting Information

Dynamic Gold(I) Complexes of Hexa-*tert*-butyl-octaphosphane

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ejic201901300-sup-0001-SupMat.pdf

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2. Experimental Section

General Remarks

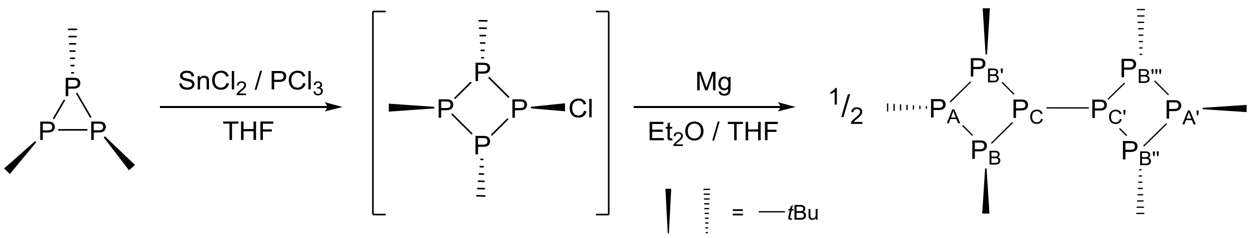
All experiments were carried out under nitrogen using standard Schlenk techniques. Toluene, dichloromethane, diethyl ether, pentanes as well as hexanes (isomeric mixtures) and acetonitrile were dried and degassed with an MB SPS-800 Solvent Purification System (MBRAUN) and kept over molecular sieves (4 Å). THF was distilled from potassium and benzophenone and kept over molecular sieves (4 Å). The compounds *cyclo*-(P_3tBu$_3$)[1] and [AuCl(tht)][2] were prepared as described in the literature. Magnesium turnings were activated by heating to about 500 °C under vacuum. Cooling baths for temperatures of –83 °C were prepared from ethyl acetate and liquid nitrogen. All other chemicals were purchased and used without further purification.

Elemental Analysis. A VARIO EL (HERAEUS) microanalyzer was used to determine the elemental composition of the compounds.

Infra-red Spectroscopy. Samples were prepared as KBr pellets in a nitrogen-filled glove box and the infrared spectra recorded in a range of 400 − 4000 cm^{-1}. A PERKIN-ELMER (System 2000) FT-IR spectrometer was used for compound **1** and a BRUKER (TENSOR 27) FT-IR spectrometer for compounds **2** to **4**. Abbreviation for labeling the vibrations: w – weak; m – medium; s – strong; δ_s – symmetric deformation vibration; δ_{as} – asymmetric deformation vibration; v_s – symmetric stretching vibration; v_{as} – asymmetric stretching vibration; ρ – Rocking vibration.

Luminescence. Luminescence was tested at 254 and 366 nm using a common UV lamp.

Synthesis of 2,2',3,3',4,4'-Hexa-*tert*-butyl-1,1'-bicyclotetraphosphane {*cyclo*-(P_4tBu$_3$)}$_2$ (1)



1

PCl_3 (7.2 g, 52.7 mmol, 1.0 eq) was added to a freshly prepared solution of $SnCl_2$ (10.0 g, 52.7 mmol, 1.0 eq) in 140 mL in THF. This solution was immediately added dropwise to a solution of *cyclo*-(P_3tBu$_3$) (13.9 g, 52.7 mmol, 1.0 eq) in 220 mL THF at –83 °C over the course of about 15 min. Subsequently, the reaction mixture was stirred for one hour at room temperature and kept at 5 °C overnight, resulting in the formation of crystals of $SnCl_4(THF)_2$. Evaporation of the solvent under reduced pressure gave a yellowish solid which was extracted with 500 mL pentanes twice. Removal of the solvent of the combined phases gave a viscous yellowish oil which was dried under vacuum and then dissolved in a mixture of 450 mL Et_2O and 50 mL THF. This solution was added to magnesium turnings (1.5 g, 62.1 mmol, 1.1 eq) and stirred overnight. The solvents were removed under reduced pressure and the residue extracted with 500 mL hexanes three times. Removal of the combined phases under reduced pressure gave a raw product which was separated by fractionated crystallization as follows:

1. Suspending in 150 mL boiling THF and decantation after 5 min gave a small crystal fraction of pure phosphane **1** after one day which was separated by filtration and washed with 10 mL Et_2O.
2. Keeping the filtrate at –30 °C gave pure octaphosphane **1** as a colorless crystalline solid after six days which was separated by filtration and washed with 20 mL Et_2O.

Yield: 4.3 g (28%, colorless crystalline solid).

MP: 253 °C (Decomp.)

$^1H\{^{31}P\}$ NMR (C_6D_6): δ = 1.33 (s, 18H, (**H**$_3$C)$_3$C-P$_A$), 1.30 (s, 36H, (**H**$_3$C)$_3$C-P$_B$) ppm.

$^{13}C\{^1H,^{31}P\}$ NMR (C_6D_6): δ = 30.6 (s, **C**-P$_A$), 30.5 (s, **C**-P$_B$), 29.0 (s, (H$_3$**C**)$_3$C-CP$_A$), 28.8 (s, (H$_3$**C**)$_3$C-CP$_B$) ppm.

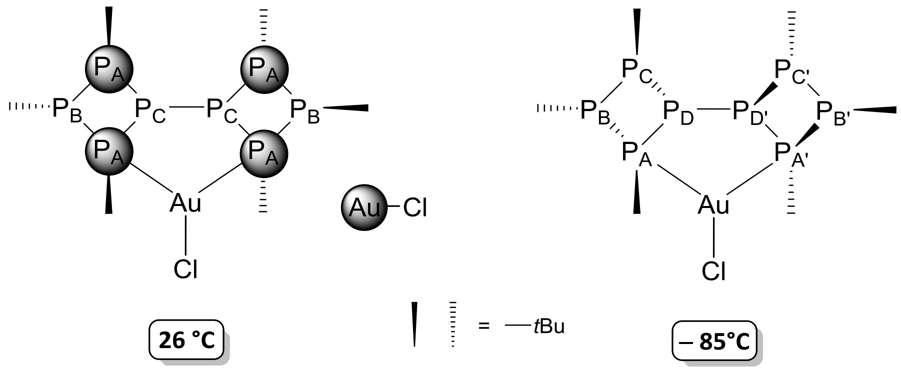
$^{31}P\{^1H\}$ NMR (C_6D_6): δ = –38.3 (m, 2P, P$_A$), –46.2 (m, 4P, P$_B$), –103.0 (m, 2P, P$_C$) ppm.

IR (KBr): $\tilde{\nu}$ = 3182 (w), 2931 (s, v_{as}(C–H)), 2852 (s, v_s(C–H)), 2705 (w), 1452 (s, $\delta_{as}(CH_3)$), 1386 (m, $\delta_s(CH_3)$), 1358 (s, $\delta_s(CH_3)$), 1172 (s, ρ(CH_3) + v_s(C–C)), 1010 (m, ρ(CH_3)), 935 (m, ρ(CH_3) + v_s(C–C)), 805 (m, v_s(C–C)), 728 (w), 574 (m), 457 (w) cm^{-1}.

MS (ESI(+), MeCN/THF 1:1): *m/z* = 239.0 $[P_4{}^tBu_2H]^+$ (5%), 255.0 $[P_4{}^tBu_2OH]^+$ (4%), 271.0 $[P_4{}^tBu_2O_2H]^+$ (1%), 287.0 $[P_4{}^tBu_2O_3H]^+$ (2%), 303.0 $[P_4{}^tBu_2O_4H]^+$ (1%), 327.1 $[P_5{}^tBu_3H]^+$ (4%), 343.1 $[P_5{}^tBu_3OH]^+$ (4%), 359.1 $[P_5{}^tBu_3O_2H]^+$ (3%), 375.1 $[P_5{}^tBu_3O_3H]^+$ (4%), 391.1 $[P_5{}^{t}Bu_3O_4H]^+$ (1%), 407.1 $[P_5{}^{t}Bu_3O_5H]^+$ (1%), 415.1 $[P_6{}^{t}Bu_4H]^+$ (3%), 431.1 $[P_6{}^{t}Bu_4OH]^+$ (7%), 447.1 $[P_6{}^{t}Bu_4O_2H]^+$ (2%), 463.1 $[P_6{}^{t}Bu_4O_3H]^+$ (4%), 479.1 $[P_6{}^{t}Bu_4O_4H]^+$ (2%), 495.1 $[P_6{}^{t}Bu_4O_5H]^+$ (1%), 503.2 $[P_7{}^{t}Bu_5H]^+$ (3%), 519.2 $[P_7{}^{t}Bu_5O_1H]^+$ (26%), 535.2 $[P_7{}^{t}Bu_5O_2H]^+$ (20%), 551.2 $[P_7{}^{t}Bu_5O_3H]^+$ (3%), 567.2 $[P_7{}^{t}Bu_5O_4H]^+$ (3%), 583.1 $[P_7{}^{t}Bu_5O_5H]^+$ (2%), 599.1 $[P_7{}^{t}Bu_5O_6H]^+$ (1%), 607.2 $[P_8{}^{t}Bu_6OH]^+$ (78%), 623.2 $[P_8{}^{t}Bu_6O_2H]^+$ (100%), 629.2 $[P_8{}^{t}Bu_6ONa]^+$ (14%), 639.2 $[P_8{}^{t}Bu_6O_3H]^+$ (54%), 645.2 $[P_8{}^{t}Bu_6O_2Na]^+$ (27%), 655.2 $[P_8{}^{t}Bu_6O_4H]^+$ (16%), 661.2 $[P_8{}^{t}Bu_6O_3Na]^+$ (18%), 671.2 $[P_8{}^{t}Bu_6O_5H]^+$ (1%), 677.2 $[P_8{}^{t}Bu_6O_4Na]^+$ (6%), 693.2 $[P_8{}^{t}Bu_6O_5Na]^+$ (1%), 1235.4 $[(P_8{}^{t}Bu_6)_2O_3Na]^+$ (3%), 1251.4 $[(P_8{}^{t}Bu_6)_2O_3Na]^+$ (5%), 1267.4 $[(P_8{}^{t}Bu_6)_2O_4Na]^+$ (7%), 1283.4 $[(P_8{}^{t}Bu_6)_2O_5Na]^+$ (7%), 1299.4 $[(P_8{}^{t}Bu_6)_2O_6Na]^+$ (4%), 1315.4 $[(P_8{}^{t}Bu_6)_2O_7Na]^+$ (1%), 1331.4 $[(P_8{}^{t}Bu_6)_2O_8Na]^+$ (<1%).

Elemental Analysis for $C_{24}H_{54}P_8$	Found (%)	C: 49.04	H: 9.19
	Calculated (%)	C: 48.82	H: 9.24

Synthesis of [AuCl(1)] (2)



A freshly prepared solution of [AuCl(tht)] (44 mg, 138 mmol, 1.0 eq) in 35 mL THF was added dropwise to a solution of phosphane **1** (81.4 mg, 138 mmol, 1.0 eq) in 20 mL THF over the course of two hours using a syringe pump, resulting in a pale yellow solution. The solvent was removed under reduced pressure and the residue washed with 3 mL of hexanes. The resulting yellow-greyish powder was dried in vacuum for one hour. The solid shows no luminescent behavior and good solubility in THF and toluene.

Yield: 125 mg. (98%)

MP: 199 °C (Decomp.)

$^1H\{^{31}P\}$ NMR (THF-d_8, 26 °C): δ = 1.29 (br, $(\mathbf{H}_3C)_3C\text{-}P_B$, $(\mathbf{H}_3C)_3C\text{-}P_A$) ppm.

$^1H\{^{31}P\}$ NMR (THF-d_8, –85 °C): δ = 1.28 (br, $(\mathbf{H}_3C)_3C\text{-}P_A$), 1.26 (br, $(\mathbf{H}_3C)_3C\text{-}P_B$, $(\mathbf{H}_3C)_3C\text{-}P_C$) ppm.

$^{13}C\{^1H,^{31}P\}$ NMR (THF-d_8, 26 °C): δ = 32.6 (s, $(H_3\mathbf{C})_3C\text{-}CP_A$), 31.2 (s, $(H_3\mathbf{C})_3C\text{-}CP_B$), 28.8 (s, $(H_3\mathbf{C})_3C\text{-}CP_B$) ppm, 27.9 (s, $(H_3\mathbf{C})_3C\text{-}CP_A$).

$^{31}P\{^1H\}$ NMR (THF-d_8, 26 °C): δ = –15.8 (m, 4P, P_A), –32.2 (m, 2P, P_B), –78.9 (m, 2P, P_C) ppm.

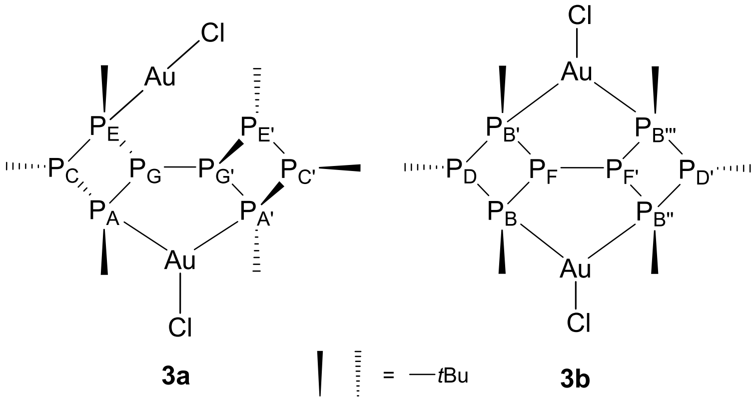
$^{31}P\{^1H\}$ NMR (THF-d_8, –85 °C): δ = 16.3 (m, 2P, P_A), –39.1 (m, 2P, P_B) –45.1 (m, 2P, P_C), –81.5 (m, 2P, P_D) ppm.

IR (KBr): $\tilde{\nu}$ = 3436 (m), 2947 (s, ν_{as}(C–H)), 2890 (s, ν_s(C–H)), 2855 (s, ν_s(C–H)), 1631 (w), 1457 (s, $\delta_{as}(CH_3)$), 1388 (m, $\delta_s(CH_3)$), 1361 (s, $\delta_s(CH_3)$), 1261 (w), 1171 (s, $\rho(CH_3)$ + ν_s(C–C)), 1151 (s), 1012 (w, $\rho(CH_3)$, 937 (w, $\rho(CH_3)$ + ν_s(C–C)), 804 (m, ν_s(C–C)), 616 (w), 573 (w), 541 (w), 523 (w), 494 (w), 423 (w) cm^{-1}.

MS (ESI(+), MeCN/THF 1:1): *m/z* = 673.0 $[P_8{}^{t}Bu_4Au]^+$ (44%), 677.2 $[LO_4Na]^+$ (53%), 693.2 $[LO_5Na]^+$ (10%), 709.2 $[LO_6Na]^+$ (1%), 787.2 $[LAu]^+$ (100%), 803.2 $[LOAu]^+$ (5%). L = $C_{24}H_{54}P_8$.

Elemental Analysis for $C_{24}H_{54}AuClP_8$	Found (%)	C: 36.30	H: 6.76
	Calculated (%)	C: 35.03	H: 6.61

Synthesis of [$(AuCl)_2$(1)] (3)



A freshly prepared solution of [AuCl(tht)] (80 mg, 250 mmol, 2.0 eq) in 35 mL THF was added dropwise to a solution of phosphane **1** (74 mg, 125 mmol, 1.0 eq) in 20 mL THF over the course of 1.5 hours using a syringe pump, resulting in a pale yellow solution. About 50 mL of the solvent were removed under reduced pressure and a yellow solid precipitated. The solid was filtered off, washed with 2 mL of hexanes and dried in vacuum for one hour. The filtrate was reduced to 1 mL under reduced pressure. Gas diffusion of hexanes over night at 0 °C gave a yellow crystalline solid which was filtered off, washed with 2 mL of hexanes and dried in vacuum for one hour. Both solids are analytically identical and were combined. The solid shows no luminescent behavior and is slightly soluble in THF and toluene. Single crystals were obtained from passing a stream of dry nitrogen over a saturated solution of the complex in THF.

Yield: 111 mg (84%)

MP: 231 °C (Decomp.)

$^{1}H\{^{31}P\}$ NMR (THF-*d*$_8$): δ = 1.40 – 1.15 (various s, C**H**$_3$) ppm.

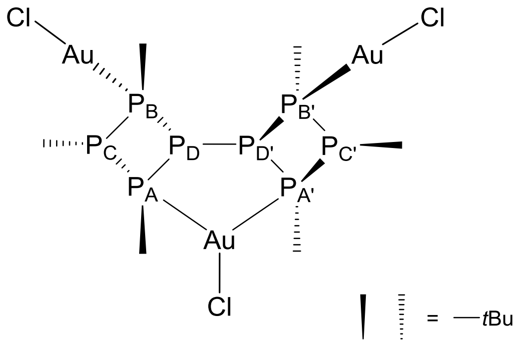
$^{31}P\{^{1}H\}$ NMR (THF-*d*$_8$, 25 °C): δ = 20.5 (m, 2P, P_A), –3.0 (m, P_B), –24.0 (m, 2P, P_C), –29.7 (m, P_D), –48.5 (m, 2P, P_E), –63.3 (m, P_F), –73.3 (m, 2P, P_G) ppm. (The signals P_A, P_C, P_E and P_G correspond to **3b**. The remaining signals possess significantly lower intensity and are assigned to **3a**.)

IR (KBr): $\tilde{\nu}$ = 3445 (s), 2952 (s, ν_{as}(C–H)), 2892 (s, ν_s(C–H)), 2857 (s, ν_s(C–H)), 1723 (w), 1635 (m), 1459 (s, $\delta_{as}(CH_3)$), 1387 (m, $\delta_s(CH_3)$), 1362 (s, $\delta_s(CH_3)$), 1262 (m), 1171 (s, $\rho(CH_3)$ + ν_s(C–C)), 1011 (m, $\rho(CH_3)$), 988 (m), 951 (w, $\rho(CH_3)$ + ν_s(C–C)), 803 (m, ν_s(C–C)), 713 (w), 593 (w), 542 (w), 418 (w) cm^{-1}.

MS (ESI(+), MeCN): *m/z* = 673.0 $[P_8{}^tBu_4Au]^+$ (5%), 787.2 $[LAu]^+$ (33%), 803.2 $[LAOu]^+$ (8%), 1019.1 $[LAu_2Cl]^+$ (100%), 1035.1 $[LOAu_2Cl]^+$ (2%), 1077.1 $[LAu_2Cl_2Na]^+$ (13%), 1093.1 $[LOAu_2Cl_2Na]^+$ (1%), 1251.0 $[LAu_3Cl_2]^+$ (1%). L = $C_{24}H_{54}P_8$.

Elemental Analysis for $C_{24}H_{54}Au_2Cl_2P_8$	Found (%)	C: 22.85	H: 4.07
	Calculated (%)	C: 22.39	H: 4.23

Synthesis of [$(AuCl)_3$(1)] (4)



A freshly prepared solution of [AuCl(tht)] (280 mg, 873 mmol, 3.5 eq) in 30 mL THF was added dropwise to a solution of phosphane **1** (146 mg, 247 mmol, 1.0 eq) in 20 mL THF over the course of 10 minutes and stirred for one hour. About 55 mL of the solvent were removed under reduced pressure, resulting in the precipitation of a yellow solid. The solid was filtered off, washed with 3 mL of hexanes and dried in vacuum for one hour. The filtrate was reduced to 1 mL under reduced pressure. Gas diffusion of hexanes over night at 0 °C gave a yellow solid which was filtered off, washed with 3 mL of hexanes and dried in vacuum for one hour. Both solids are analytically identical and were combined. The solid shows no luminescent behavior and is very poorly soluble in THF and toluene. Single crystals were obtained from a saturated solution of the complex in THF at 0 °C.

Yield: 268 mg (84%)

MP: 183 °C (Decomp.)

^{1}H{^{31}P} NMR (THF-*d*$_8$): δ = 1.57 (s, 18H, ($\mathbf{H}_3$C)$_3$C-P_A), 1.49 (s, 18H, ($\mathbf{H}_3$C)$_3$C-P_C), 1.44 (s, 18H, ($\mathbf{H}_3$C)$_3$C-P_B) ppm.

^{13}C{^{1}H,^{31}P} NMR (THF-*d*$_8$): δ = 28.8 (s, ($H_3\mathbf{C}$)$_3$C-CP_A), 28.5 (s, ($H_3\mathbf{C}$)$_3$C-CP_C), 26.1 (s, ($H_3\mathbf{C}$)$_3$C-CP_B) ppm. Quaternary carbon atom could not be detected.

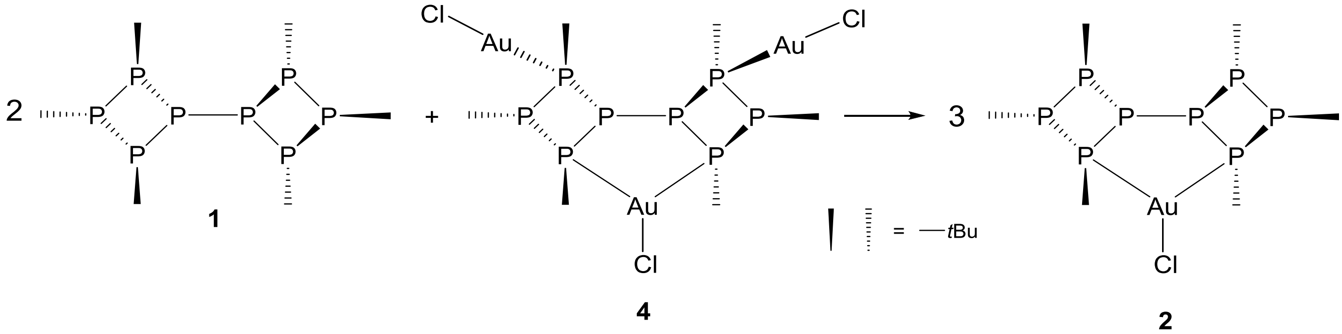
^{31}P{^{1}H} NMR (THF-*d*$_8$): δ = 12.4 (m, 2P, P_A), 9.6 (m, 2P, P_B) –20.7 (m, 2P, P_C), –45.7 (m, 2P, P_D) ppm.

IR (KBr): $\tilde{\nu}$ = 3442 (w), 2953 (s, ν_{as}(C–H)), 2891 (s, ν_s(C–H)), 2854 (m, ν_s(C–H)), 1723 (m), 1636 (m), 1544 (w), 1458 (s, $\delta_{as}(CH_3)$), 1388 (m, $\delta_s(CH_3)$), 1361 (s, $\delta_s(CH_3)$), 1262 (w), 1204 (w), 1165 (s, $\rho(CH_3)$ + ν_s(C–C)), 1102 (w), 1013 (m, $\rho(CH_3)$), 937 (w, $\rho(CH_3)$ + ν_s(C–C)), 869 (w), 802 (m, ν_s(C–C)), 668 (w), 594 (w), 541 (w), 496 (w), 418 (w) cm^{-1}.

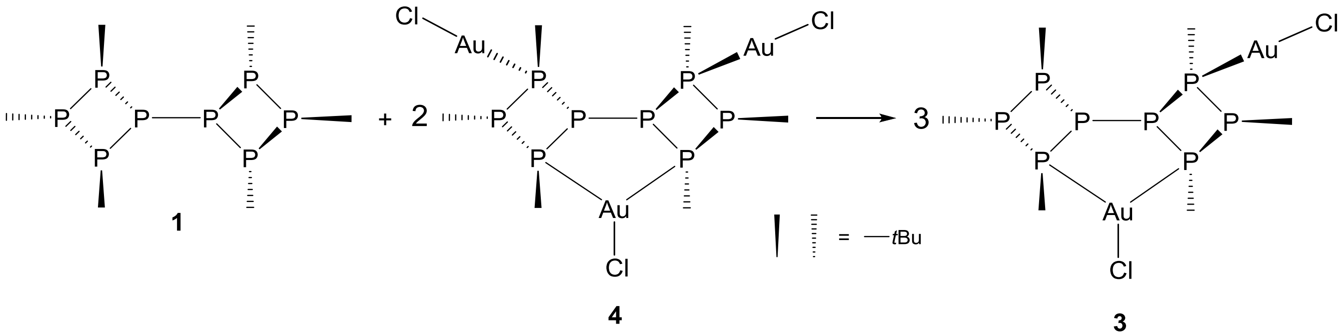
MS (ESI(+), MeCN): *m/z* = 1019.1 $[LAu_2Cl]^+$ (4%), 1251.0 $[LAu_3Cl_2]^+$ (100%), 1311.0 $[LAu_3Cl_3Na]^+$ (5%). L = $C_{24}H_{54}P_8$.

Elemental Analysis for $C_{24}H_{54}Au_3Cl_3P_8$	Found (%)	C: 27.42	H: 5.08
	Calculated (%)	C: 27.32	H: 5.16

Reactions of {*cyclo*-(P_4*t*Bu_3)}$_2$ (1) with [$(AuCl)_3$(1)] (4)

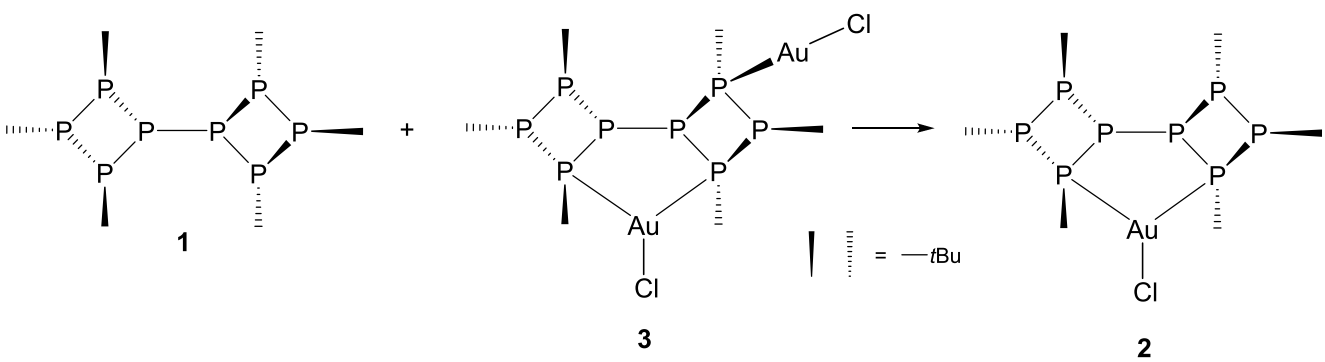


A solution of phosphane **1** (48 mg, 81 mmol, 2.0 eq) in 10 mL THF was added to a suspension of **4** (52 mg, 40 mmol, 1.0 eq) in 20 mL THF. After 5 minutes the suspension became clear and turned pale yellow. About 28 mL of the solvent were removed under reduced pressure and the reaction mixture investigated with $^{31}P\{^1H\}$ NMR spectroscopy. Removal of the solvent and drying in vacuum for 30 minutes gave a substance which was analytically identical to **2**.



A solution of phosphane **1** (15 mg, 25 mmol, 1.0 eq) in 10 mL THF was added to a suspension of **4** (64 mg, 50 mmol, 2.0 eq) in 30 mL THF. After 5 minutes the suspension became clear and turned pale yellow. About 38 mL of the solvent were removed under reduced pressure and the reaction mixture investigated with $^{31}P\{^1H\}$ NMR spectroscopy. Removal of the solvent and drying in vacuum for 30 minutes gave a substance which was analytically identical to **3**.

Reaction of {*cyclo*-(P_4*t*Bu_3)}$_2$ (1) with [$(AuCl)_3$(1)] (3)



15 mL of THF were added to a mixture of phosphane **1** (12 mg, 20 mmol, 1.0 eq) and complex **3** (21 mg, 20 mmol, 1.0 eq). The initial suspension turned clear and bright yellow after 5 minutes. About 13 mL of the solvent were removed under reduced pressure and the reaction mixture investigated with $^{31}P\{^1H\}$ NMR spectroscopy. Removal of the solvent and drying in vacuum for 30 minutes gave a substance which was analytically identical to **2**.

3. NMR Measurements and Spectra of the Compounds

NMR spectra were recorded at 25 °C with a BRUKER AVANCE DRX 400 spectrometer (^{1}H NMR: 400.13 MHz, ^{13}C NMR: 100.16 MHz, ^{31}P NMR: 161.97 MHz). TMS was used as internal standard for ^{1}H NMR spectroscopy. ^{13}C and ^{31}P NMR experiments were referenced to the Ξ scale.[3] Every signal labeling in this publication also extends to the chemically equivalent yet magnetically nonequivalent nuclei *i.e.* P_A for P_A, $P_{A'}$ as well as $P_{A''}$ and so forth. The ^{31}P NMR signals are labeled alphabetically starting from the nucleus, which is most deshielded.
All ^{31}P NMR spectra were measured with a 90° pulse and reduced acquisition (0.4 s) as well as d1 time (1.0 s). The number of scans necessary to obtain acceptable spectra strongly depended on the solubility of the respective compound. For complex **2**, usually 100 scans sufficed while at least 1000 scans were needed for the other compounds. One inversed-gated coupling ^{31}P NMR experiment for octaphosphane **1** was performed and showed approximately the same integration values as for the standard NMR experiment. Therefore, the integration values for all signals were retrieved from the standard ^{31}P NMR experiments.

NMR Spectra of 2,2',3,3',4,4'-Hexa-*tert*-butyl-1,1'-bicyclotetraphosphane {*cyclo*-(P_4*t*Bu_3)}$_2$ (1)

The spectroscopic properties of **1** differ slightly from the literature. Baudler *et al.* reported two multiplets (–45 and –100 ppm) with a relative intensity of 3:1 for the $^{31}P\{^{1}H\}$ NMR spectrum of the phosphane.[4] In contrast, the spectrum obtained in this work (Figure S2 shows three multiplets at –38.2, –46.0 and –103.0 ppm with an I_{rel} of 1:2:1 and very strong higher order effects. In the proton-coupled ^{31}P NMR spectrum, the signals P_A and P_B (Figure S3) are significantly broadened because of the $^{3}J_{PH}$ coupling of the attached ^{t}Bu groups (12.4 and 13.0 Hz as determined from the two pseudo-doublets observed in the ^{1}H NMR spectrum). Due to the lack of this coupling, the signal P_C at –103.0 ppm is thus identified as the γ-P atom which is also in accordance with the chemical shift (strong shielding). On the basis of a $^{31}P\{^{1}H\}$-$^{31}P\{^{1}H\}$ COSY NMR spectrum, signal P_B can be assigned as the phosphorus atoms in β position which also matches its relative intensity. Additionally, the results from the $^{1}H\{^{31}P\}$ NMR (two singlets with I_{rel} = 2:1) and $^{13}C\{^{31}P\}$ NMR spectra (two sets of singlets) agree with these assignments. These finding are therefore consistent with the expected AA'B_2'B'$_2$CC' spin system.

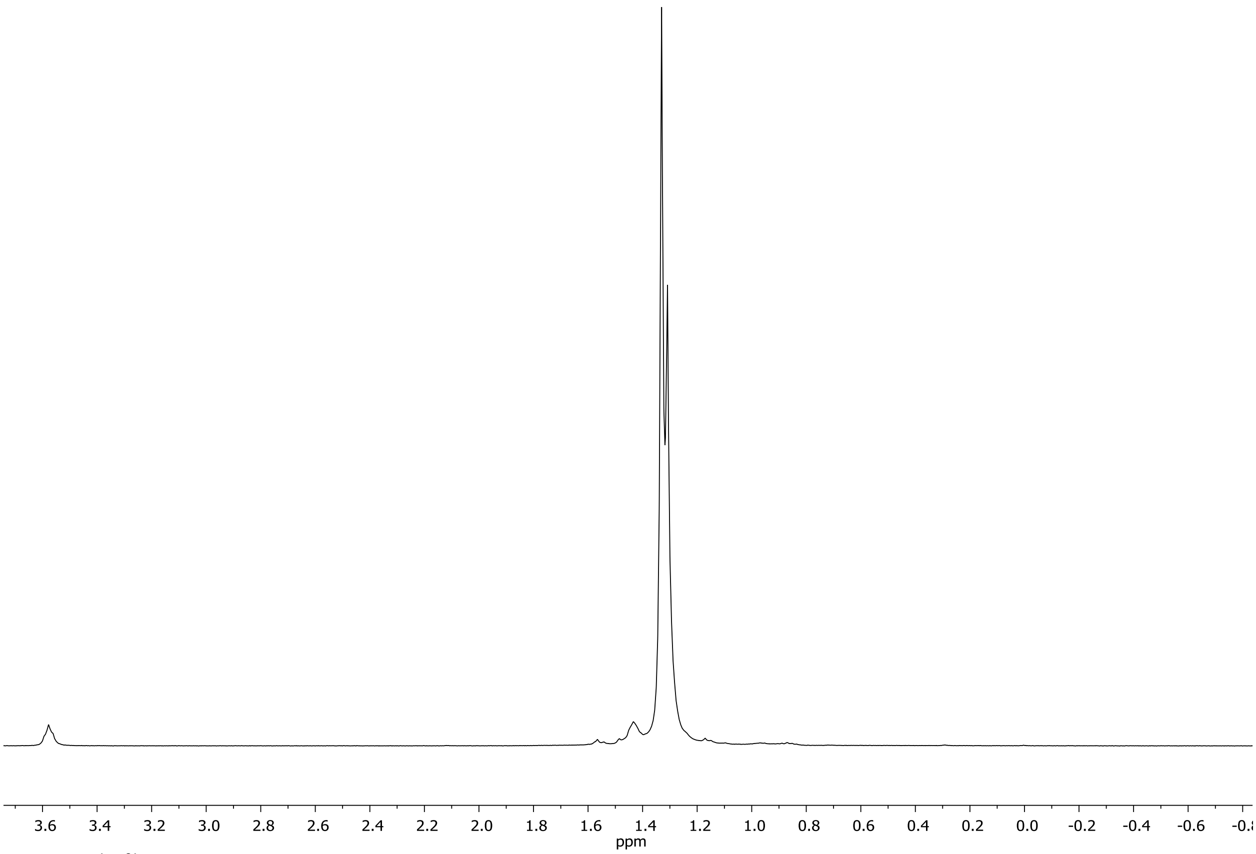


Figure S1. $^{1}H\{^{31}P\}$ NMR spectrum of phosphane **1** in THF-*d*$_8$.

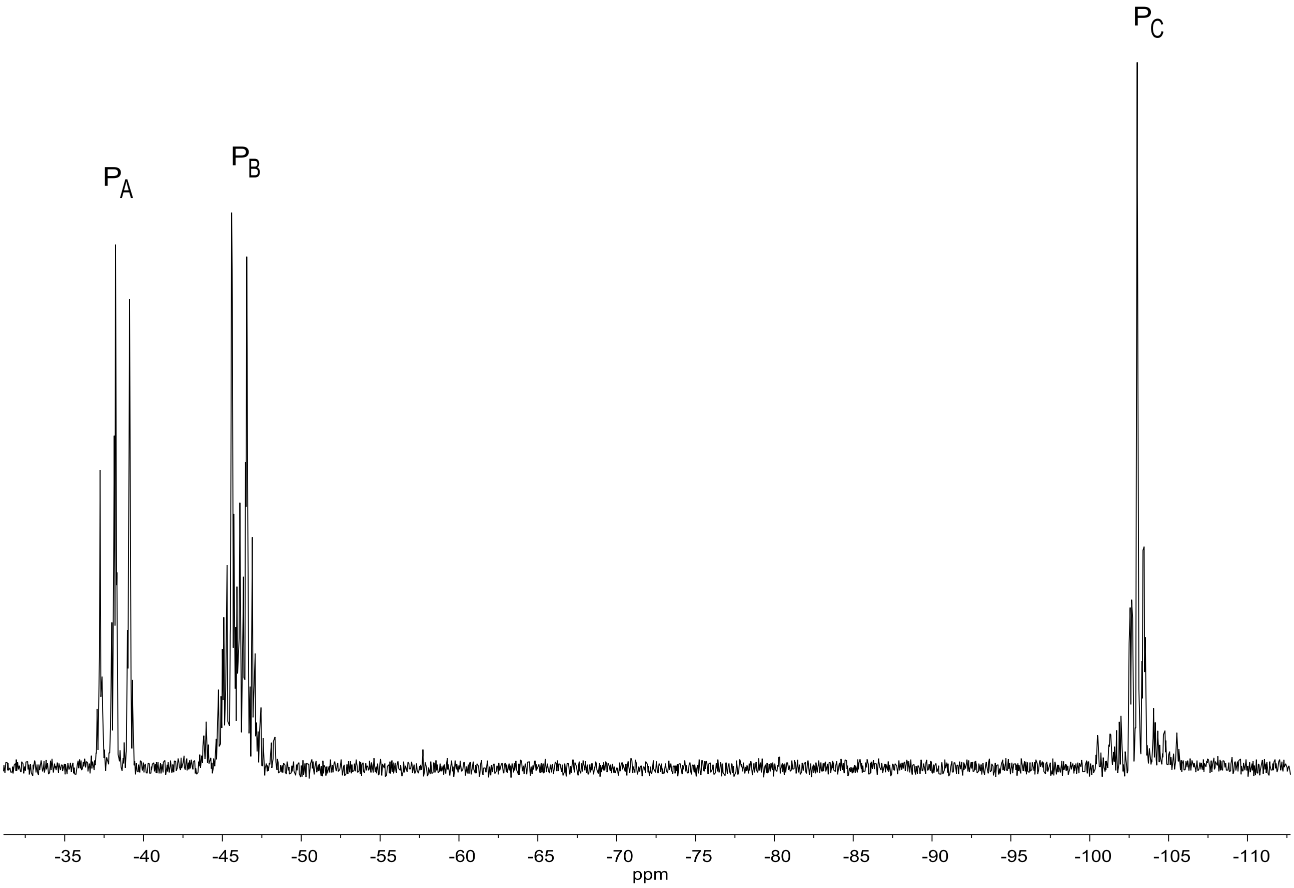


Figure S2. $^{31}P\{^1H\}$ NMR spectrum of phosphane **1** in C_6D_6.

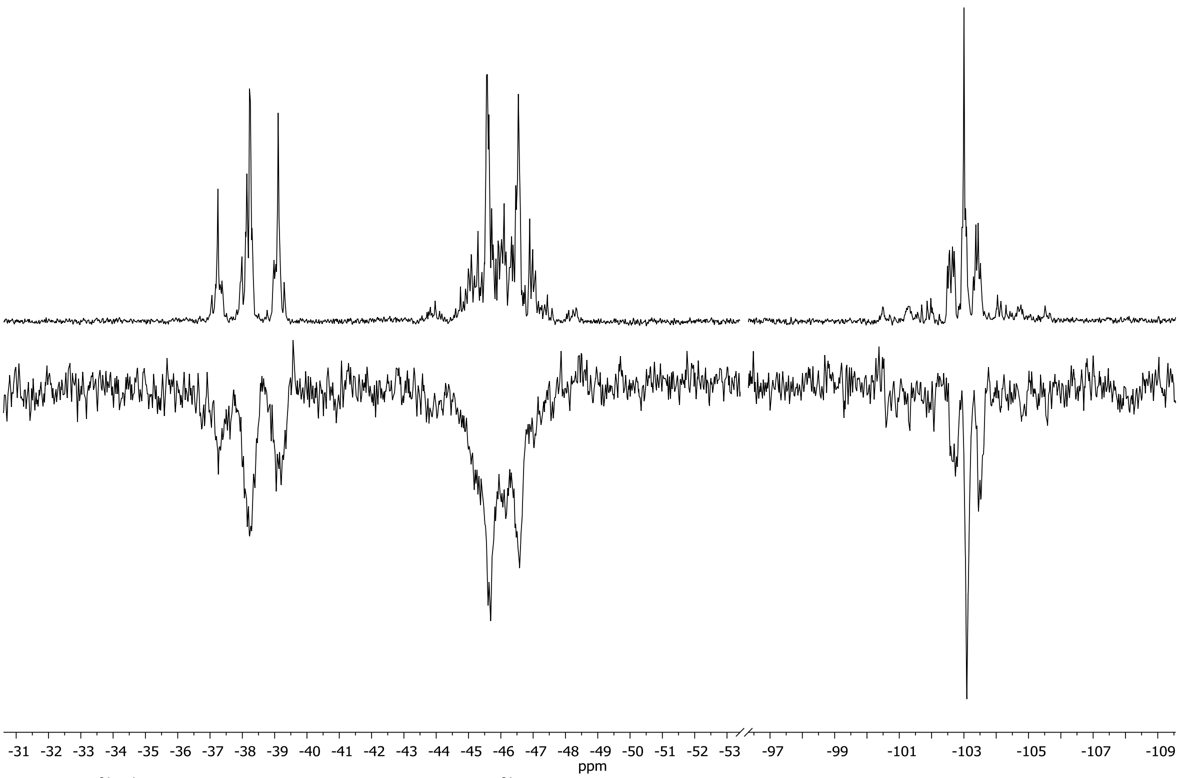


Figure S3. $^{31}P\{^1H\}$ NMR spectrum (top) and proton coupled ^{31}P NMR spectrum (bottom) of phosphane **1** in C_6D_6.

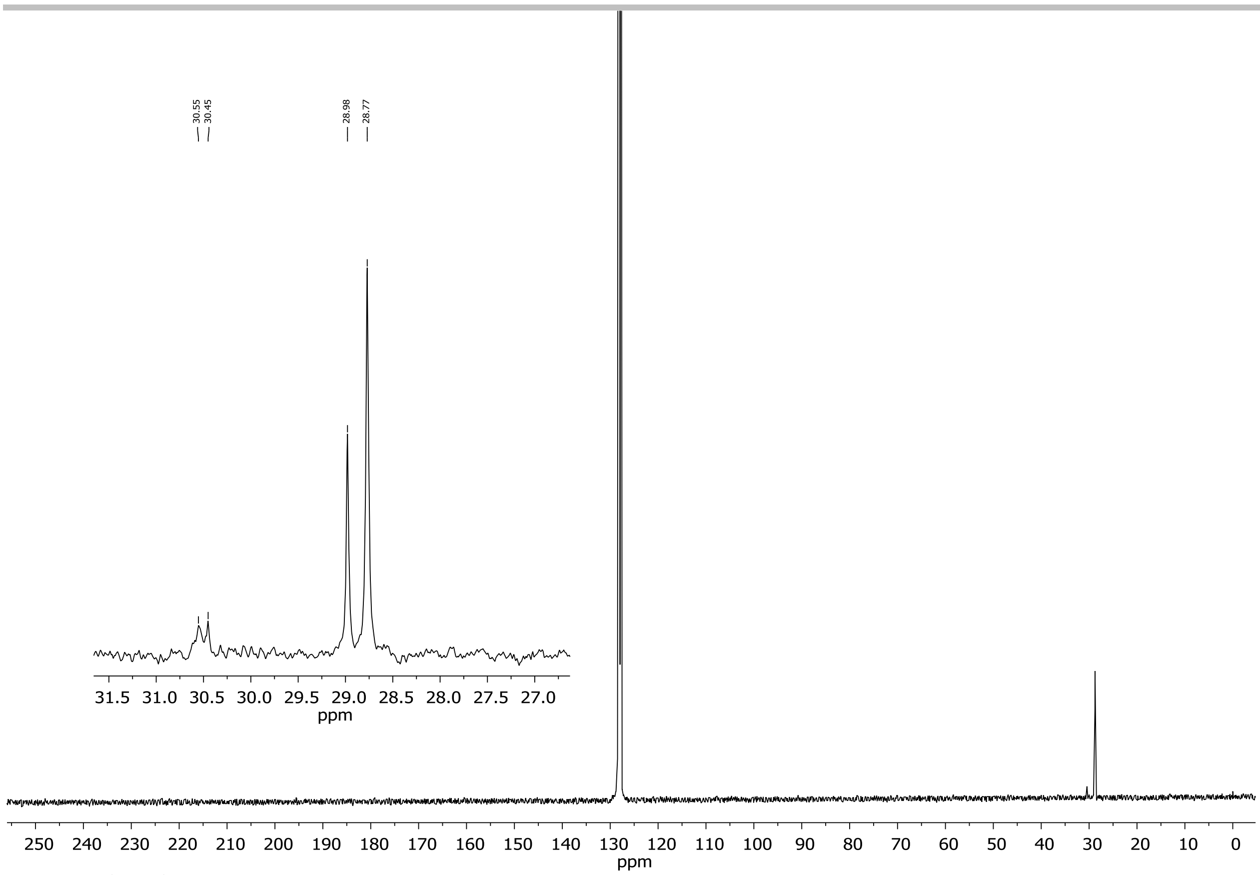


Figure S4. $^{13}C\{^{1}H,^{31}P\}$ NMR spectrum of phosphane **1** in C_6D_6.

NMR Spectra of [AuCl(1)] (2)

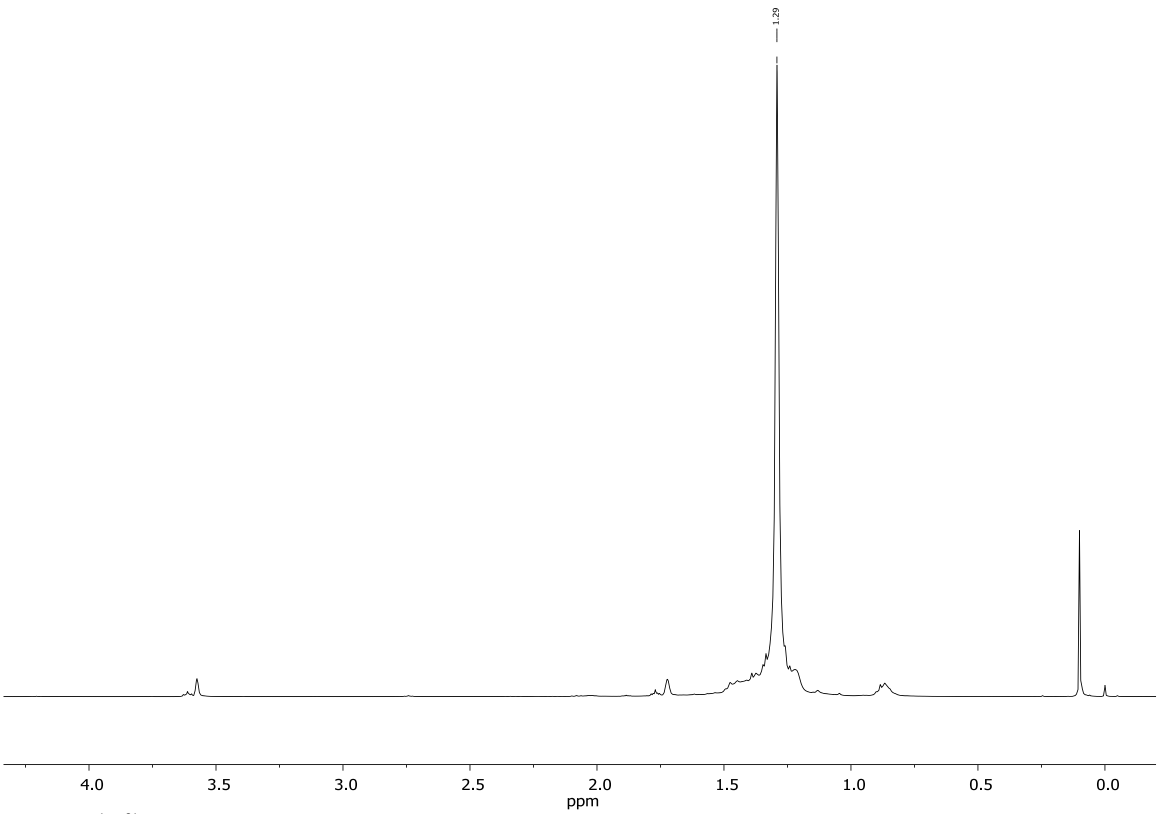


Figure S5. $^{1}H\{^{31}P\}$ NMR spectrum of complex **2** in THF-d_8 at 26 °C.

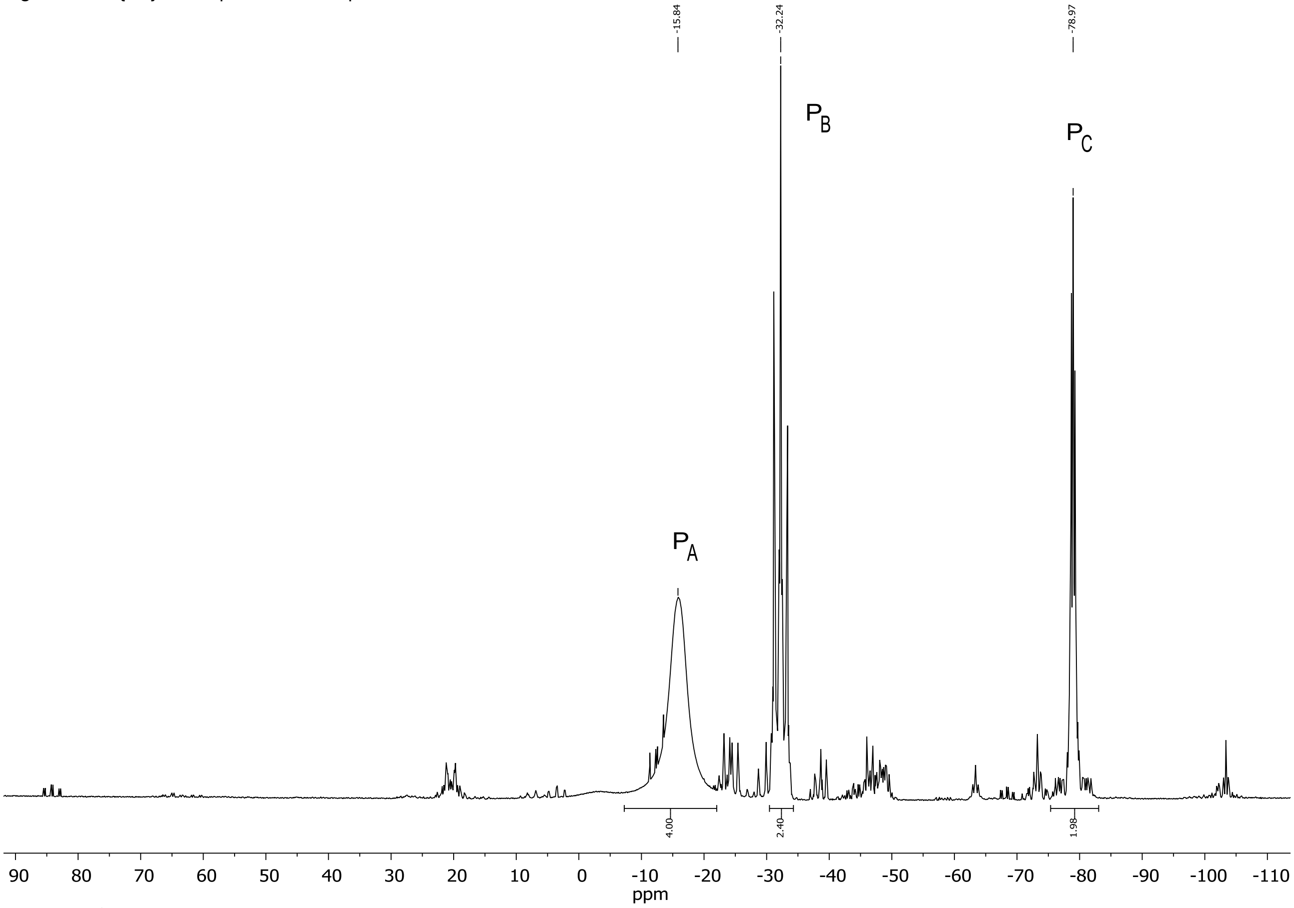


Figure S6. $^{31}P\{^{1}H\}$ NMR spectrum of complex **2** in THF-d_8/C_6D_6 at 26 °C.

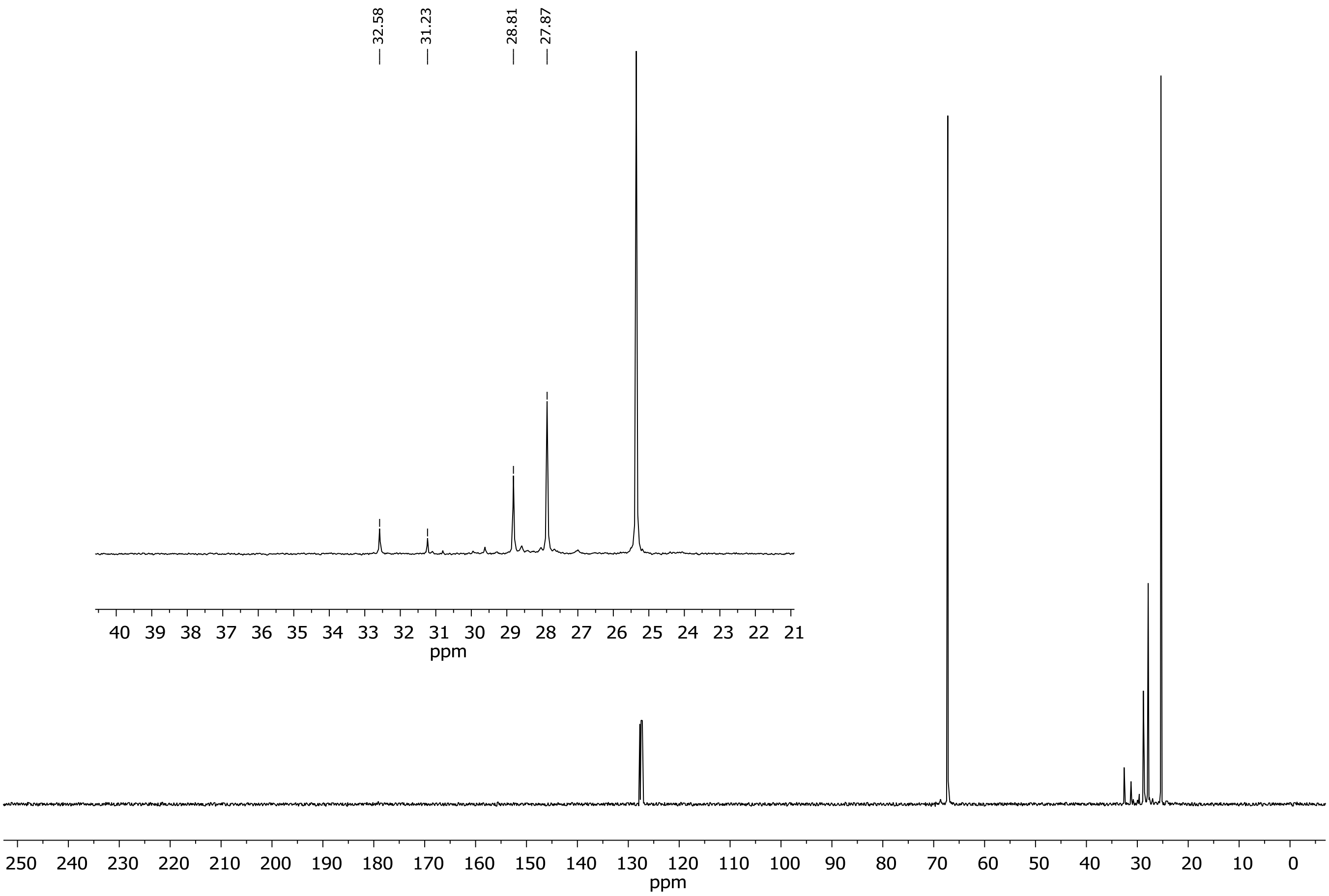


Figure S7. $^{13}C\{^{1}H,^{31}P\}$ NMR spectrum of complex **2** in THF-d_8/C_6D_6 at 26 °C.

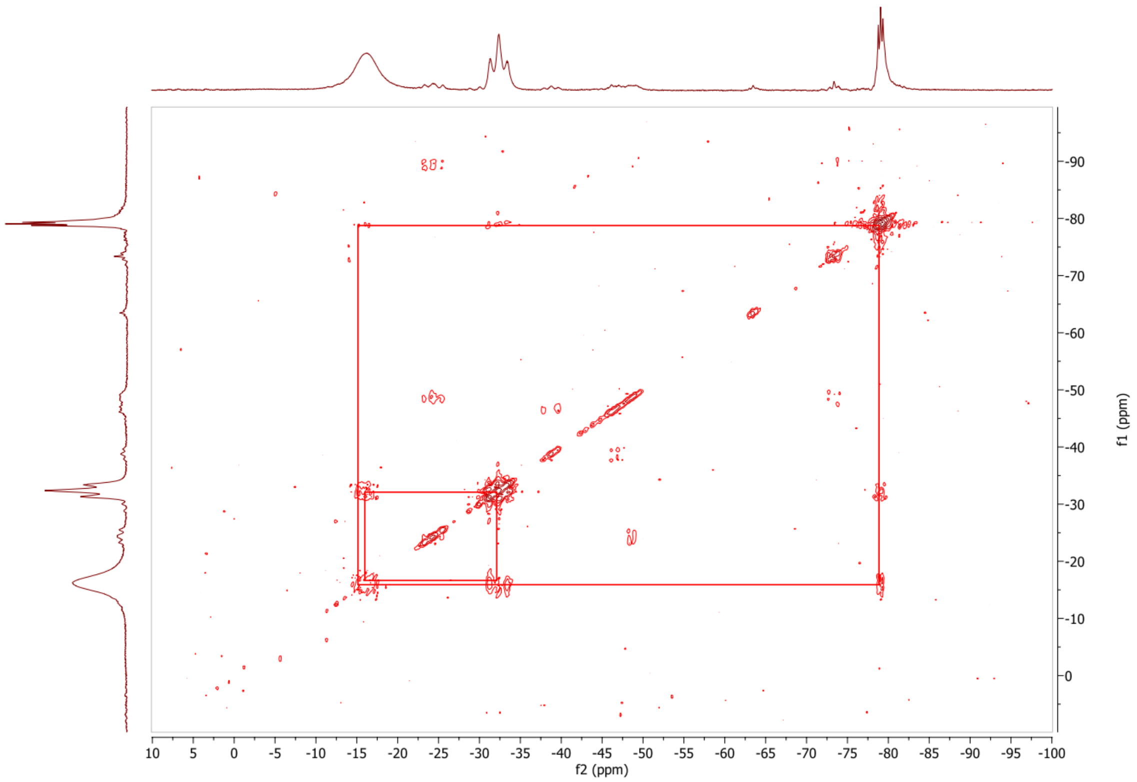


Figure S8. $^{31}P\{^{1}H\}$-$^{31}P\{^{1}H\}$ COSY NMR spectrum of complex **2** in THF-d_8/C_6D_6 at 26 °C.

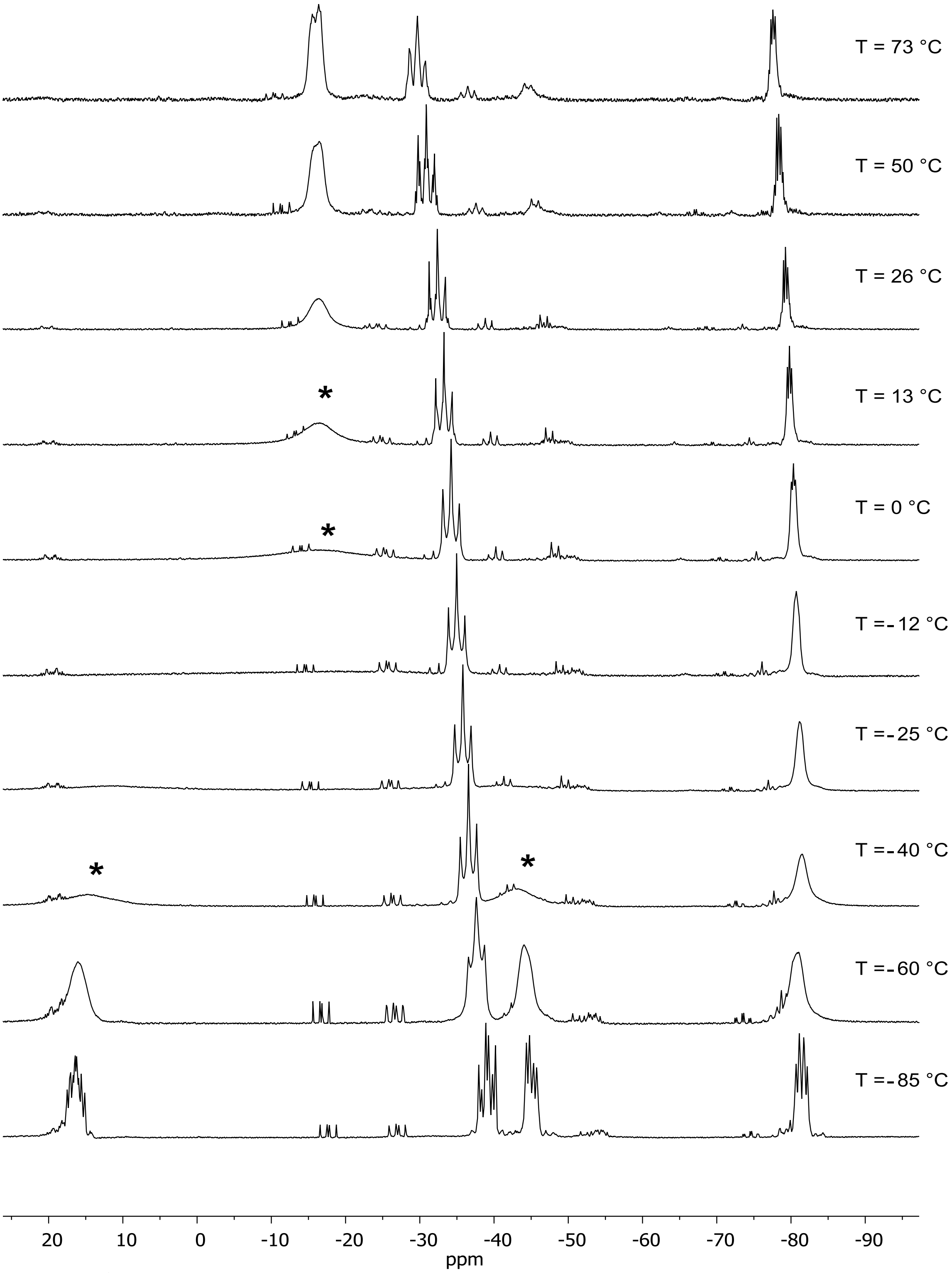


Figure S9. VT $^{31}P\{^1H\}$ NMR spectrum of complex **2** in THF-d_8/C_6D_6. The asterisks mark the decoalescing and emerging signals.

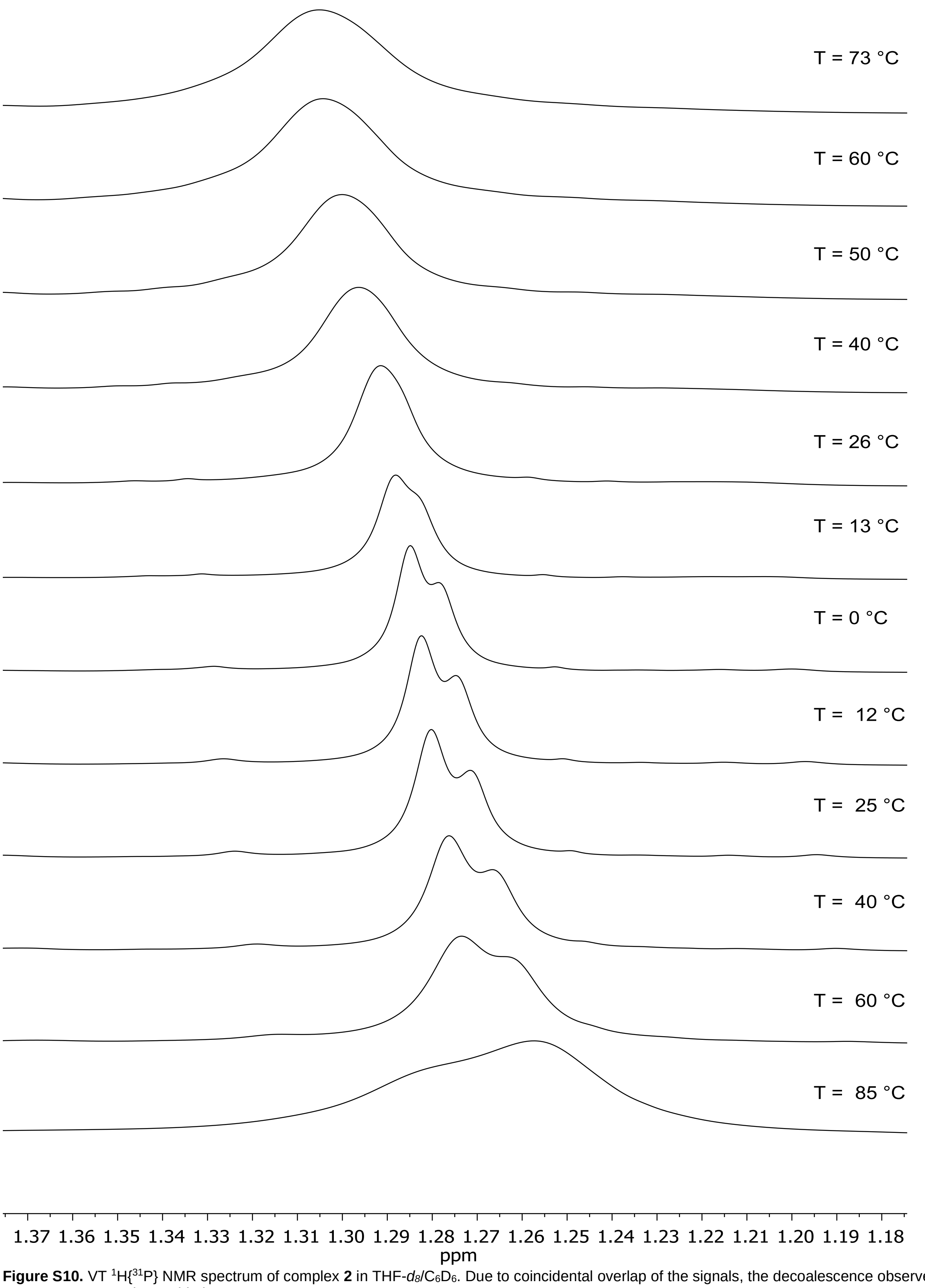


Figure S10. VT $^{1}H\{^{31}P\}$ NMR spectrum of complex **2** in THF-d_8/C_6D_6. Due to coincidental overlap of the signals, the decoalescence observed in the $^{31}P\{^{1}H\}$ NMR spectrum was not observable here.

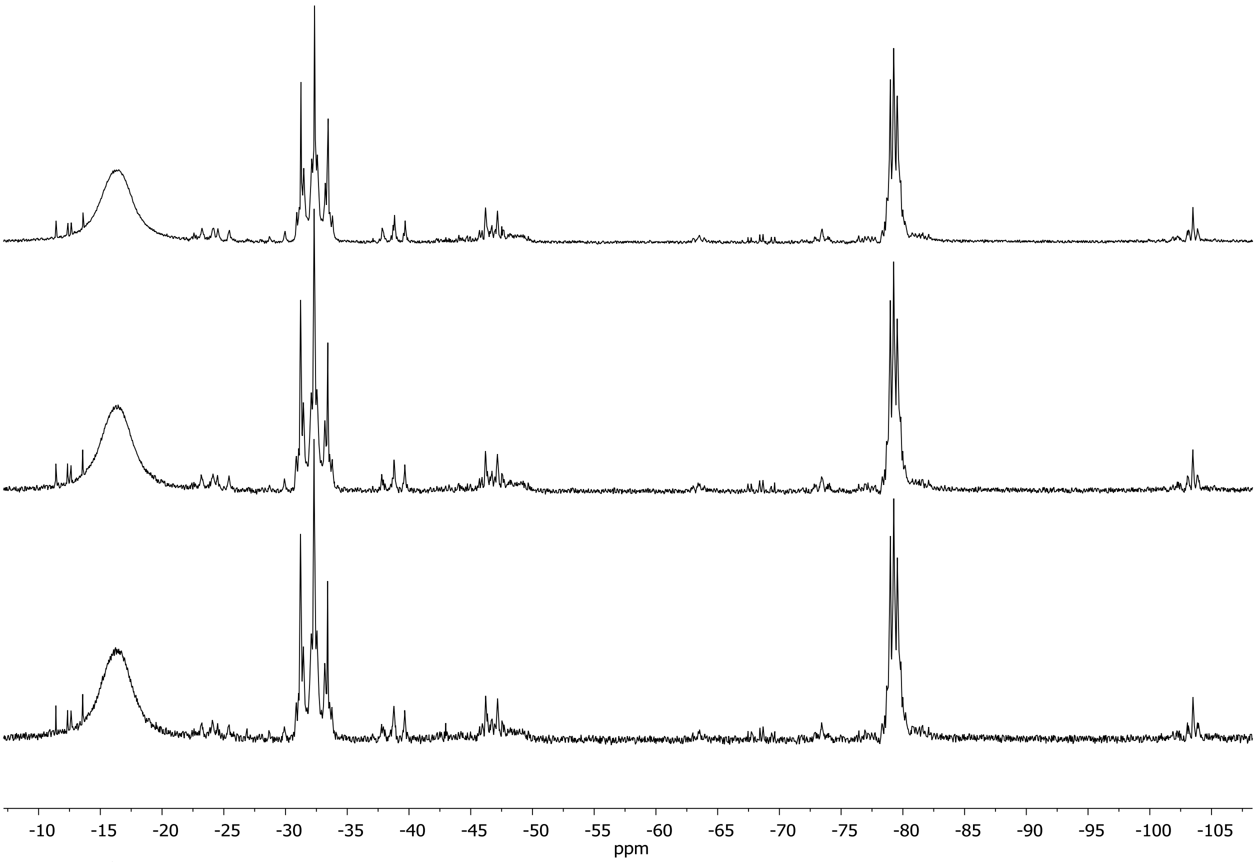


Figure S11. $^{31}P\{^{1}H\}$ NMR spectra of complex **2** in THF/C_6D_6 at **26 °C** in concentrated solution (top) and diluted with THF-d_8 factor 1.7 (middle) as well as factor 3.3 (bottom). The spectra are virtually identical.

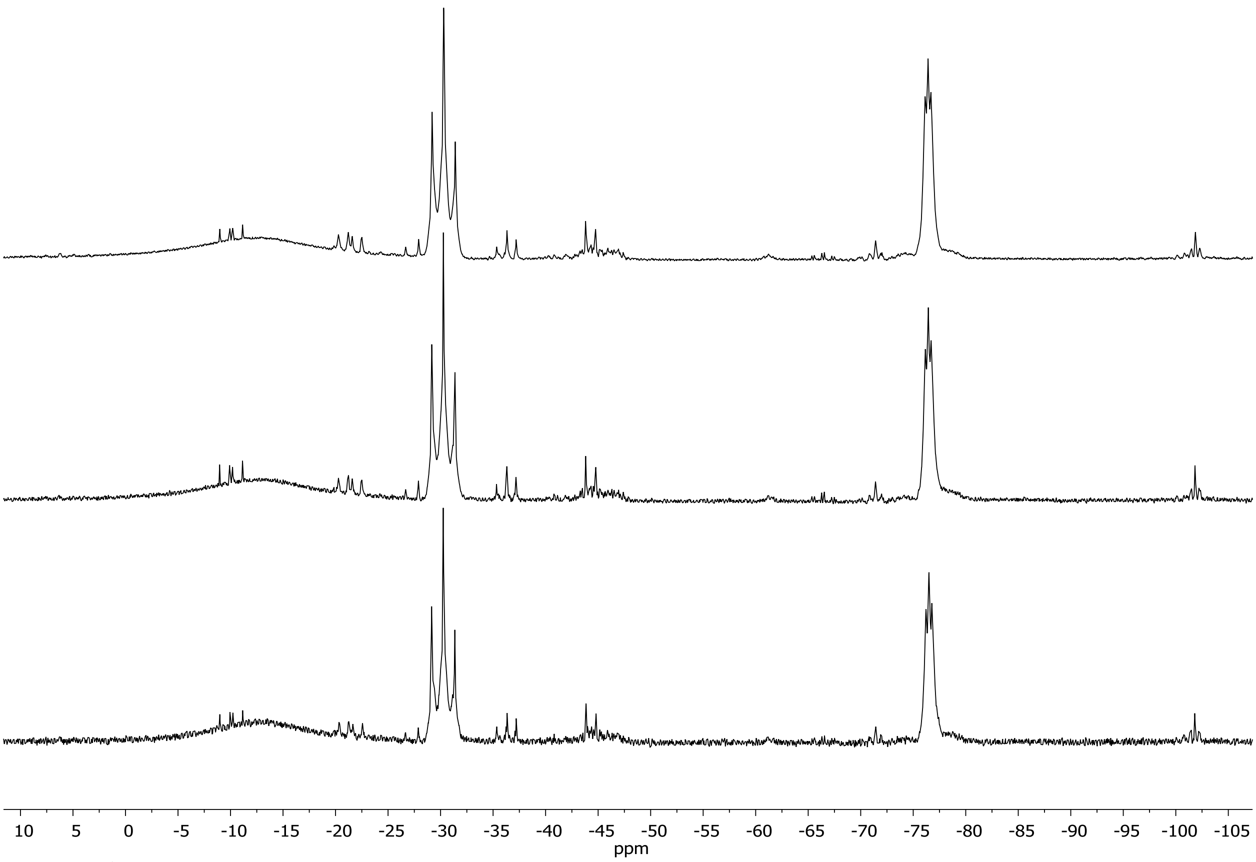


Figure S12. $^{31}P\{^{1}H\}$ NMR spectra of complex **2** in THF/C_6D_6 at **0 °C** in concentrated solution (top) and diluted with THF-d_8 factor 1.7 (middle) as well as factor 3.3 (bottom). The spectra are virtually identical.

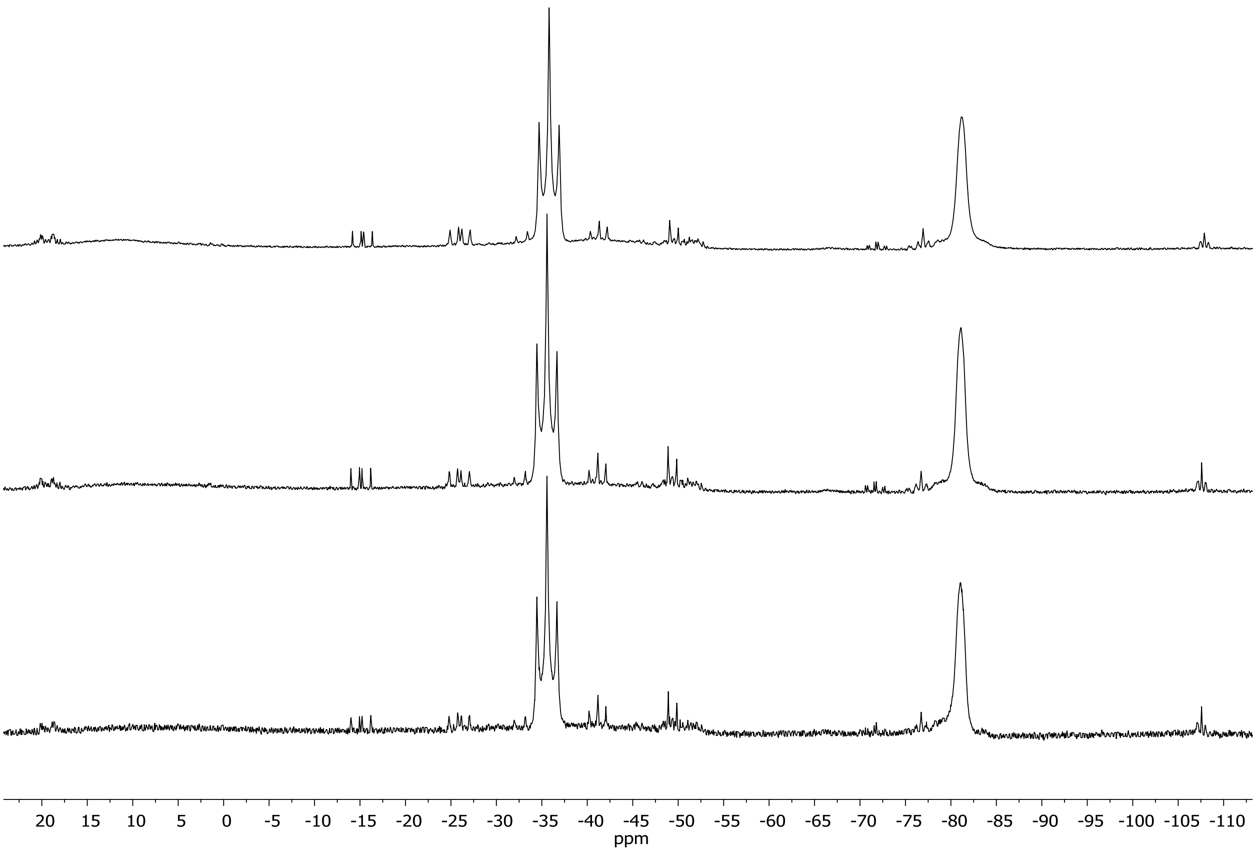


Figure S13. $^{31}P\{^{1}H\}$ NMR spectra of complex **2** in THF/C_6D_6 at **–25 °C** in concentrated solution (top) and diluted with THF-d_8 factor 1.7 (middle) as well as factor 3.3 (bottom). The spectra are virtually identical.

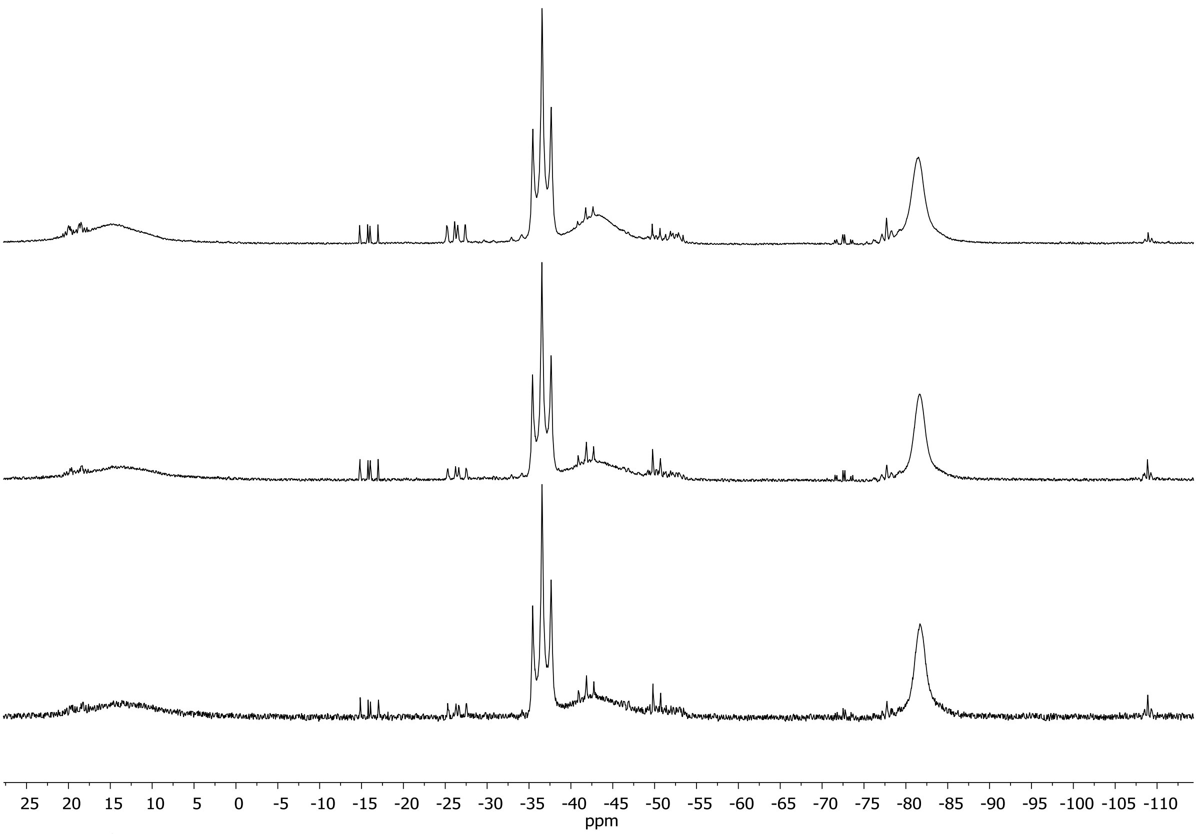


Figure S14. $^{31}P\{^{1}H\}$ NMR spectra of complex **2** in THF/C_6D_6 at **–40 °C** in concentrated solution (top) and diluted with THF-d_8 factor 1.7 (middle) as well as factor 3.3 (bottom). The spectra are virtually identical.

NMR Spectra of [(AuCl)$_2$(1)] (3)

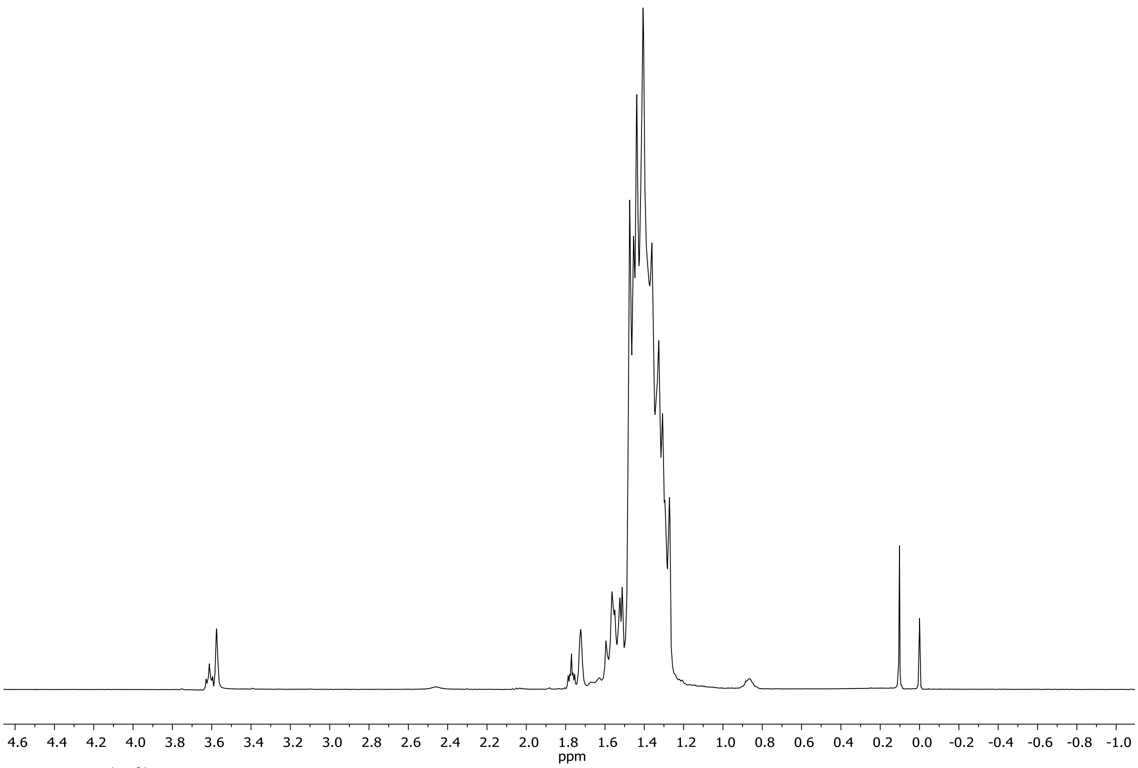


Figure S15. $^{1}H\{^{31}P\}$ NMR spectrum of complex **3** in THF-d_8.

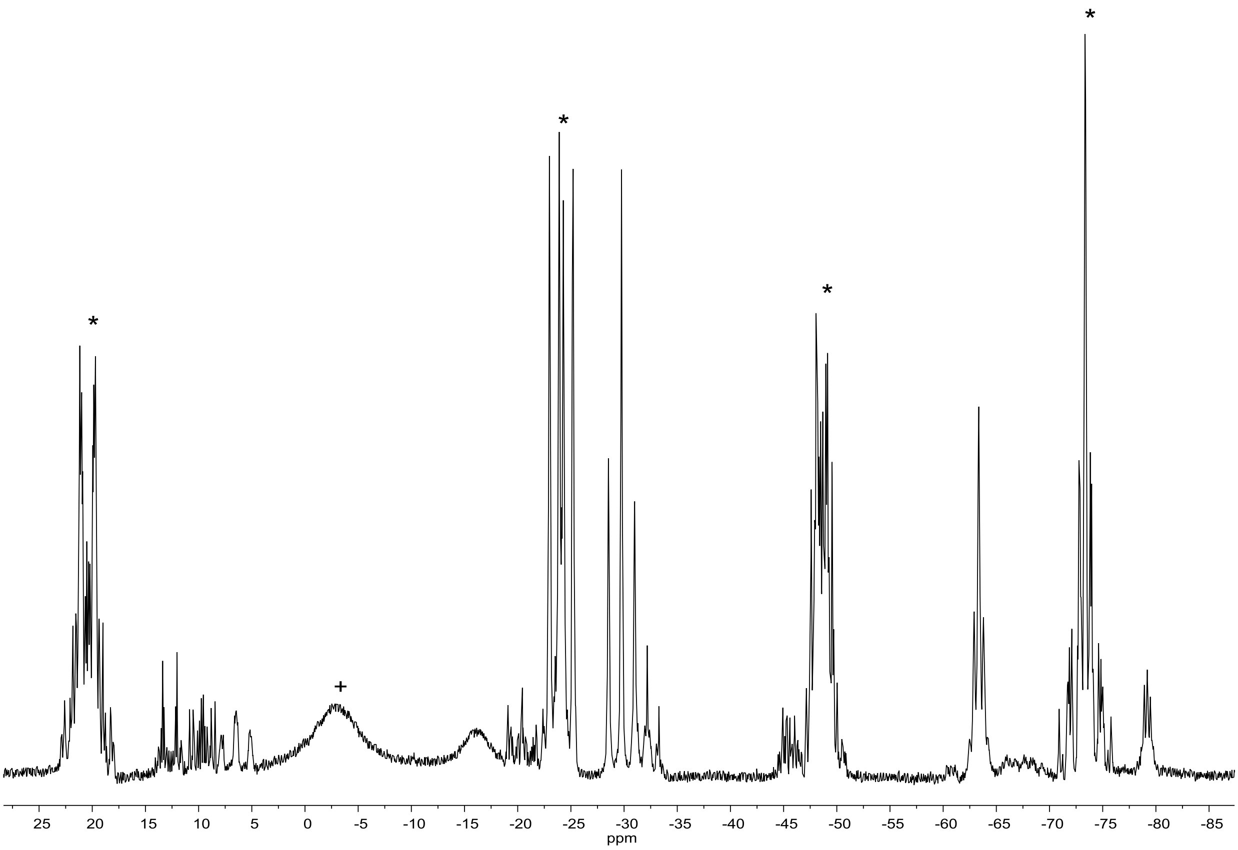


Figure S16. $^{31}P\{^{1}H\}$ NMR spectrum of complex **3** in THF-d_8. Two sets of signals for the conformers **3a** (*) and **3b** (+) are labeled. Also signals for phosphane **1**, complex **2** and **4** can be detected.

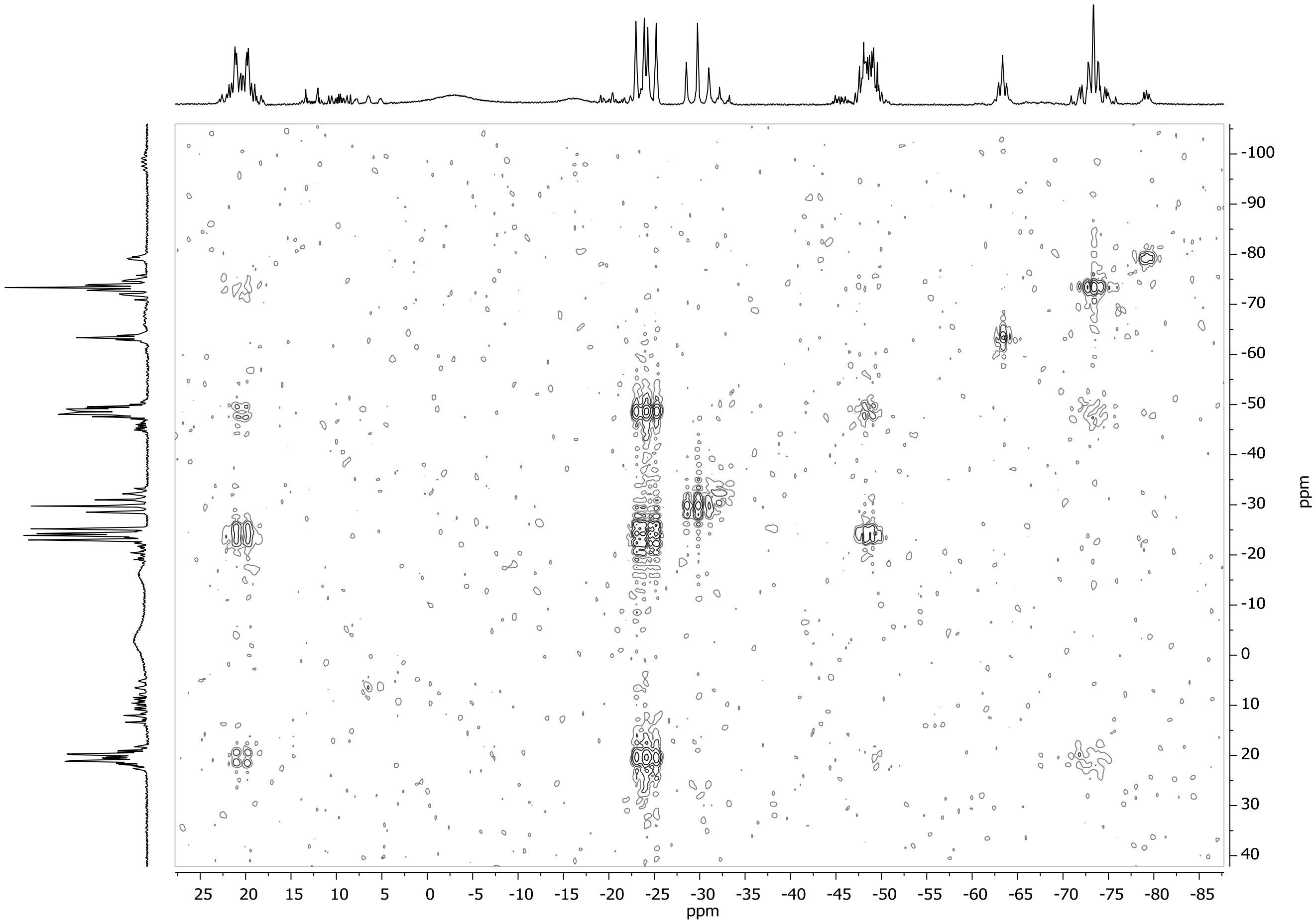


Figure S17. $^{31}P\{^{1}H\}$-$^{31}P\{^{1}H\}$ COSY NMR spectrum of complex **3** in THF-d_8.

NMR Spectra of [(AuCl)$_3$(1)] (4)

The $^{31}P\{^{1}H\}$ NMR spectrum of complex **4** (Figure S19) shows four symmetrical multiplets which are well compatible with an AA'BB'CC'DD' spin system. No information concerning the assignment of the P atoms to the structure could be retrieved from proton-coupled ^{31}P or $^{31}P\{^{1}H\}$-$^{31}P\{^{1}H\}$ COSY NMR spectroscopy. It is likely that the multiplet at –45.2 ppm corresponds to the γ-P atoms as it is most shielded. Likewise, the two multiplets at lower field (+12.7 and +9.7 ppm) belong to the coordinating β-P atoms. No change in the spectrum is observed when measuring VT NMR until –80 °C.

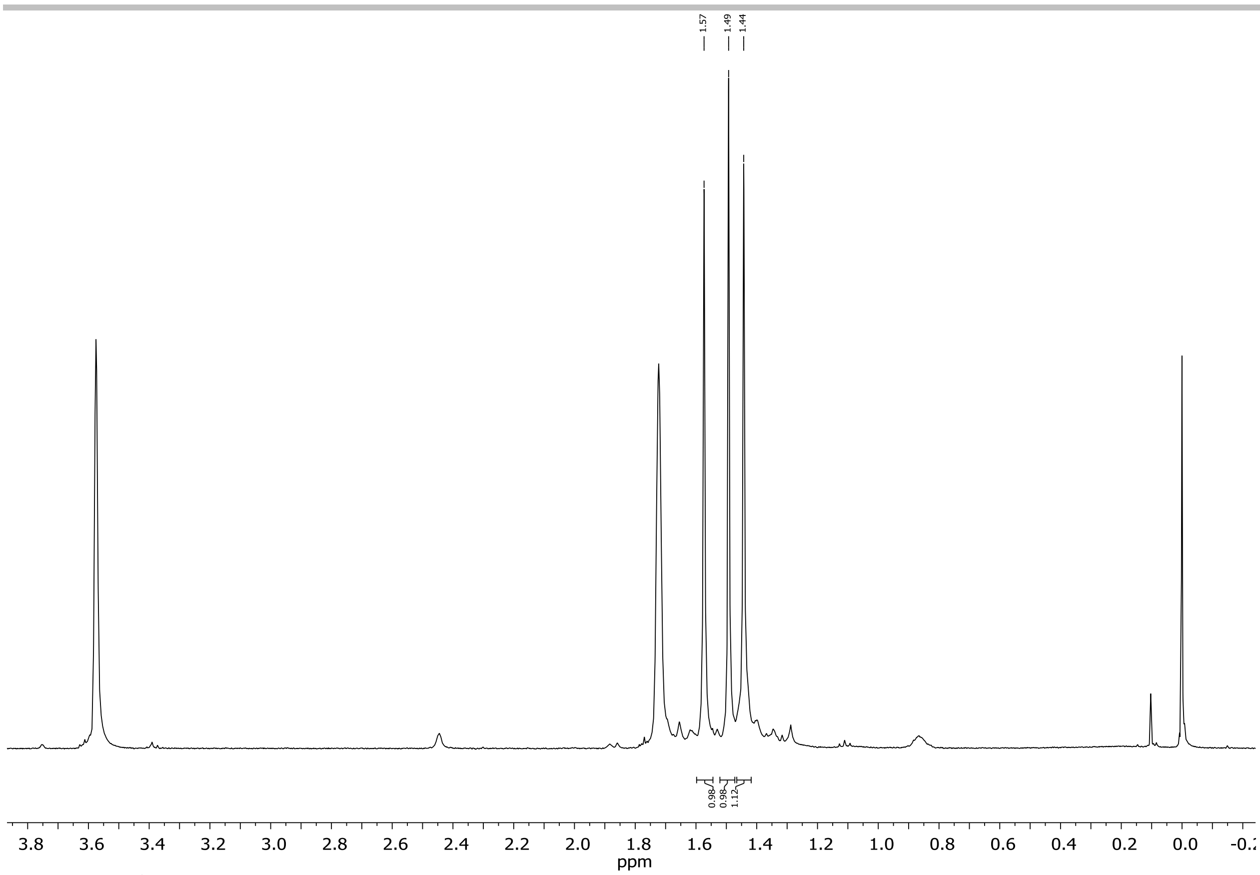


Figure S18. $^{1}H\{^{31}P\}$ NMR spectrum of complex **4** in THF-d_8.

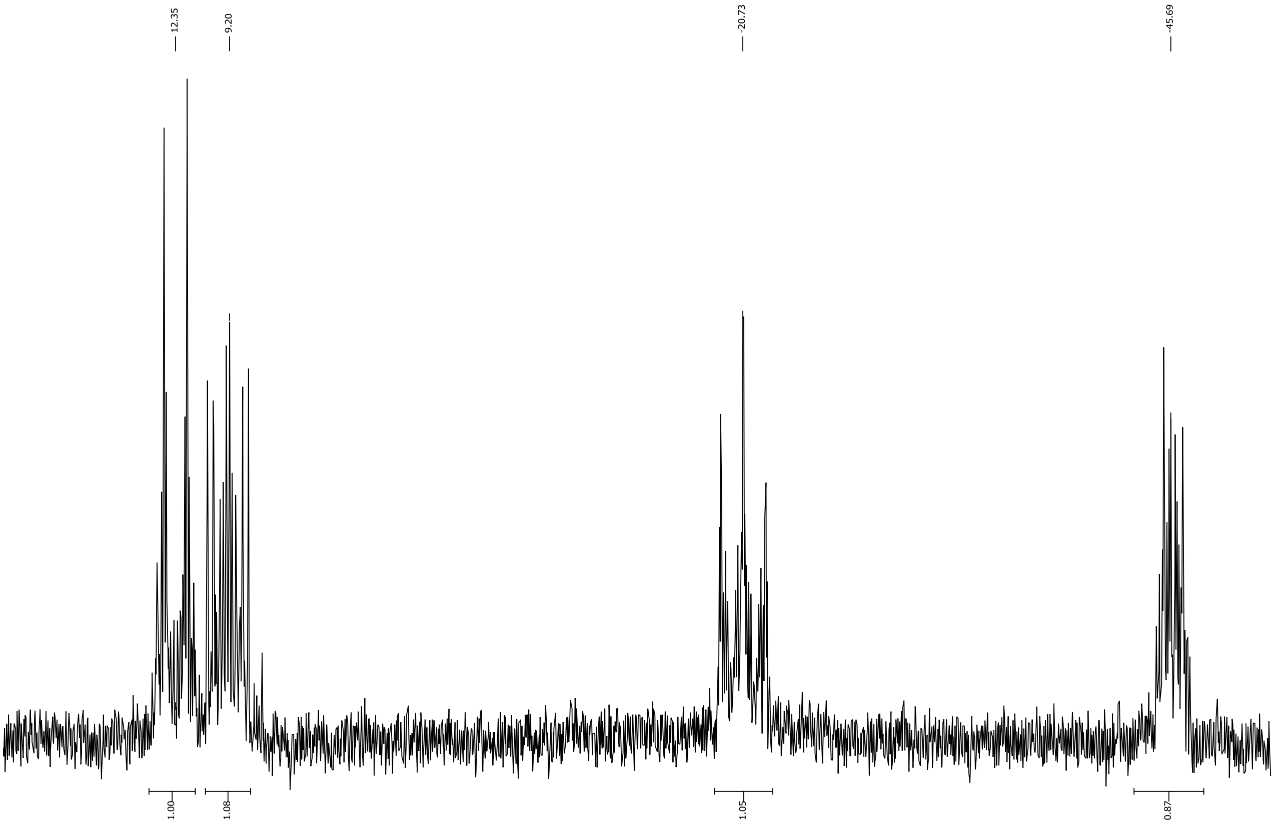


Figure S19. $^{31}P\{^{1}H\}$ NMR spectrum of complex **4** in THF-d_8.

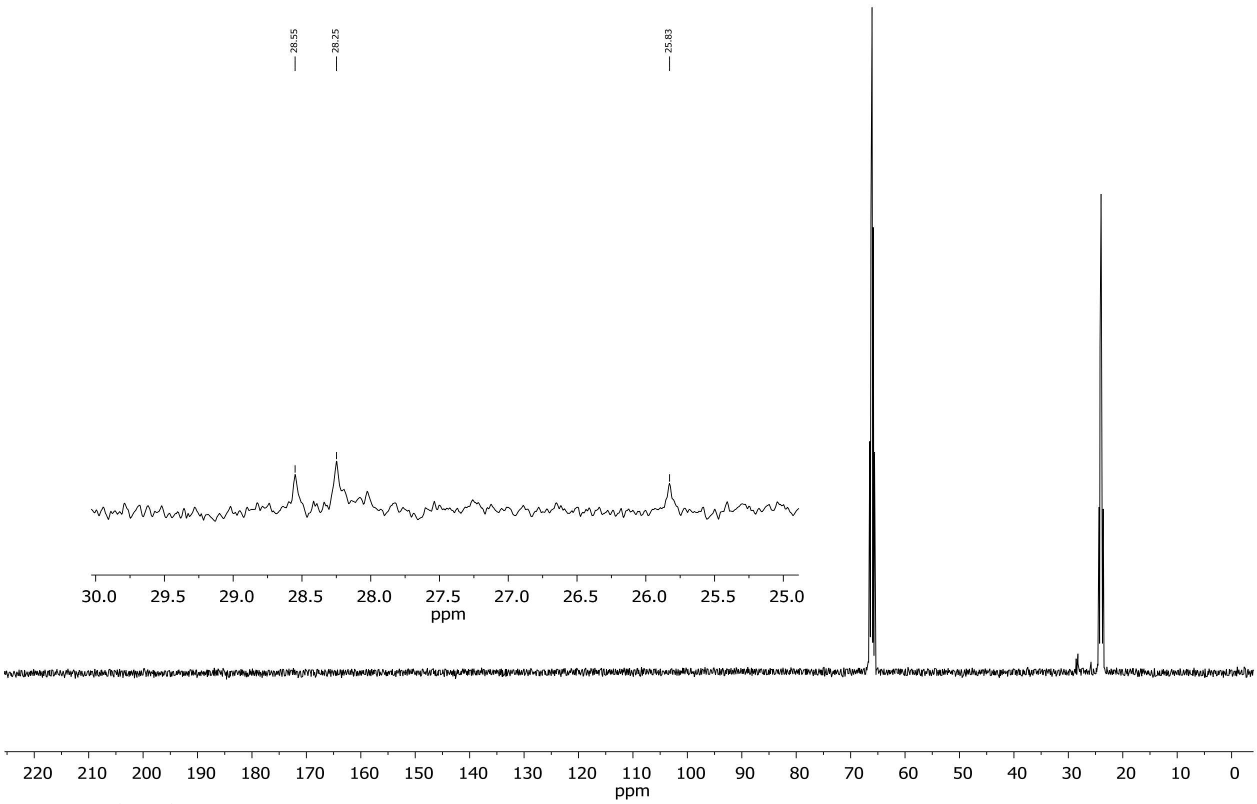


Figure S20. $^{13}C\{^1H,^{31}P\}$ NMR spectrum of complex **4** in THF-d_8.

NMR Spectra of Reaction Mixtures

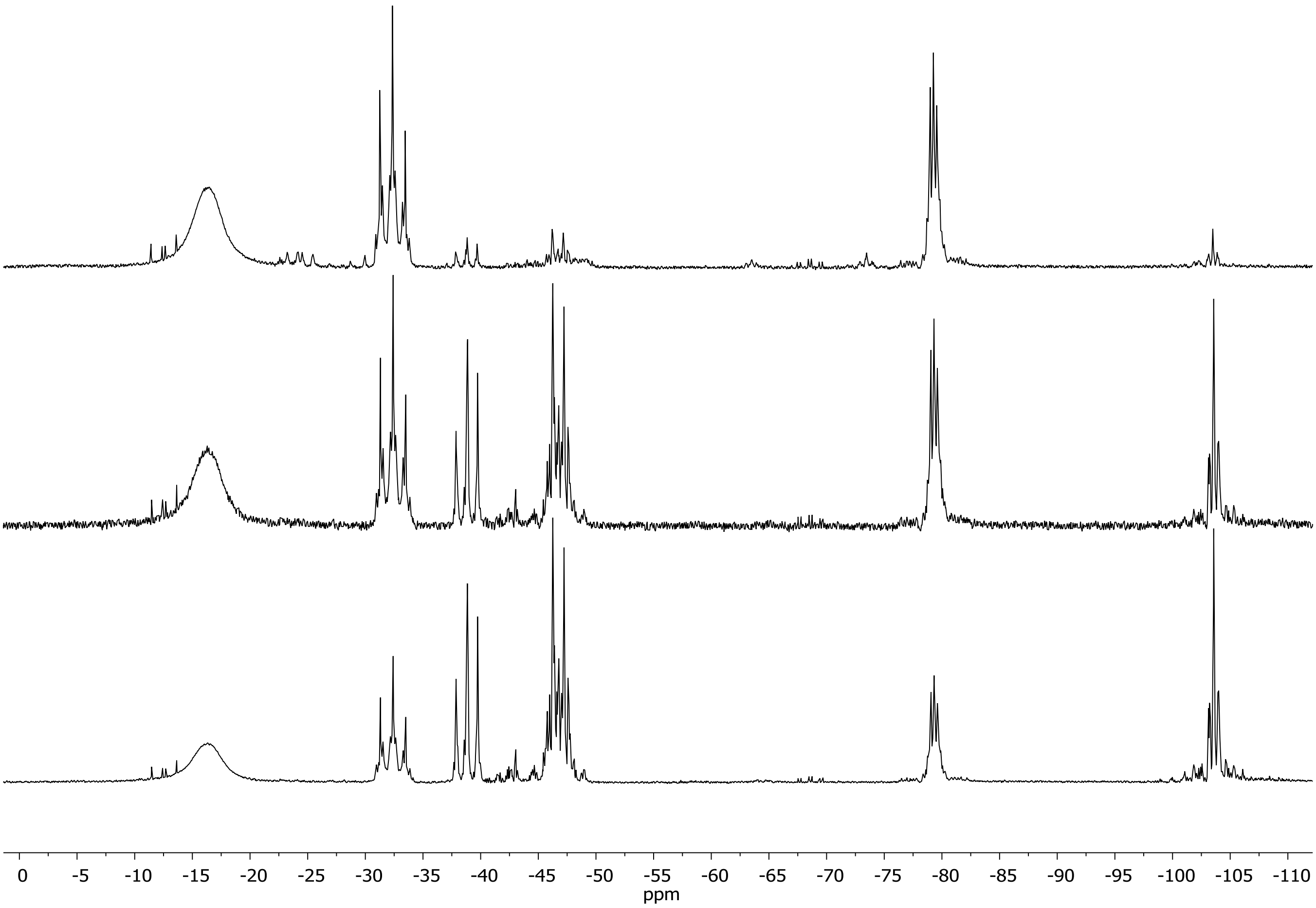


Figure S21. $^{31}P\{^{1}H\}$ NMR spectra of the reaction of phosphane **1** with 1.0 eq. of [AuCl(tht)] (top), 0.7 eq. of [AuCl(tht)] (middle) and 0.3 eq of [AuCl(tht)] (bottom) in THF/C_6D_6.

4. Mass spectrometry measurements

Mass spectrometry measurements were carried out as ESI-MS with a BRUKER DALTONICS FT-ICR-MS spectrometer (Type APEX II, 7 Tesla).

The identity of **1** is supported by mass spectrometry. Two ions attributable to the monoxide of **1** are detected as adducts with H^+ or Na^+, respectively. They occur together with the higher oxides as a series of six peaks $[M(P_8{}^tBu_6O_x)]^+$ (M = H, Na; x = 1–6) separated by *m/z* = 16. These characteristic series of peaks were also observed for all complexes containing **1** as a ligand. No peaks for $[M(P_8{}^tBu_6O_x)]^+$ ions with x = 7 or 8 are detectable. This is in accordance with the literature, as Baudler *et al.* reported that $P_8{}^tBu_6$ can be oxidized to the hexoxide but no further.[5] Obviously, the tendency of the P atoms that carry no ^{t}Bu group to be oxidized is extremely low. Another signal series that can be assigned to $[Na(P_8{}^tBu_6)_2O_x]^+$ with x = 2–9 is found. No peak for the unoxidized phosphane is detectable. This could be due to lower ionization efficiency for the parent phosphane **1** or because it is swiftly oxidized under the conditions of the MS measurement.

5. X-Ray Diffraction

Single Crystal Measurements

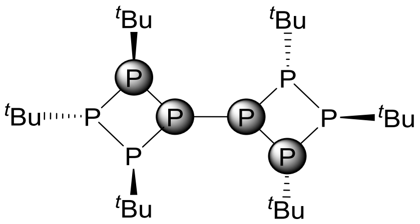
Single crystal X-ray diffraction data were collected with a GEMINI CCD diffractometer (RIGAKU). The radiation source was a molybdenum anode (Mo-K_α, $\lambda = 0.71073$ Å). The absorption corrections were carried out semiempirically with the SCALE3 ABSPACK module.[6] All structures were solved by dual space methods with Sir-92.[7] Structure refinement was done with SHELXL-2015[8] by using full-matrix least-square routines against F^2. All hydrogen atoms were calculated on idealized positions. The pictures were generated with the program ORTEP3.[9] In all pictures, hydrogen atoms were omitted for clarity and thermal ellipsoids are shown with 50% probability. CCDC 1946813 (**1**), CCDC 1946817 (**3**) and CCDC 1946818 (**4**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via https://summary.ccdc.cam.ac.uk/structure-summary-form (or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44)1223-336-033; or deposit@ccdc.cam.ac.uk). Refinement special details are

- For the crystal structure of **1**: One symmetry-independent THF molecule could be detected in the unit cell but all attempts to refine it failed. Therefore, the SQUEEZE[10] routine (PLATON) was used. This showed a solvent-accessible void of 334 Å^3 and 160 electrons per unit cell which fits well with four THF molecules per unit cell resulting in two THF molecules per phosphane molecule. A solvent-free solid-state structure of **1** has already been reported previously.[11]
- For the crystal structure of **3**: The crystal was non-merohedrally twinned. The model was refined with the twin law {–1 0 0 / 0 –1 0 / 0 0 1} which can be interpreted as a twofold rotation about [0 0 1]. The twin scale factor was refined to 0.48523. The cell dimensions of a single crystal of **3** was also determined at room temperature (reported in

Table S1) and showed no significant change compared to the measurement temperature (–143 °C).

- For the crystal structure of **4**: The crystal was non-merohedrally twinned. The model was refined with the twin law {0 0 1 / 0 –1 0 / 1 0 0} which can be interpreted as a twofold rotation about [1 0 –1]. The twin scale factor was refined to 0.30586. Three carbon atoms could not be refined anisotropically.

The dihedral angle τ in all molecular structures was extracted from the crystal structures as the mean value of the two dihedral angles between the two bridge phosphorus atoms and two phosphorus atoms connected to them (Figure S22).



1

Figure S22. Illustration of the determination of the dihedral angle τ.

Table S1. Summary of crystallographic data.

Molecule	{*cyclo*-($P_4{}^tBu_3$)}$_2$·2THF(**1**)	[$(AuCl)_2$(**1**)] (**3**)		[$(AuCl)_3$(**1**)] (**4**)
CCDC Number	1946813	1946817		1946818
Empirical formula	$C_{24}H_{54}P_8$	$C_{24}H_{54}Au_2Cl_2P_8$		$C_{24}H_{54}Au_3Cl_3P_8$
M_W (g·mol^{-1})	590.43	1055.26		1287.68
Temperature (K)	220(2)	130(2)	298	130(2)
Wavelength (Å)	0.71073	0.71073	0.71073	0.71073
Crystal system	Orthorhombic	Monoclinic		Monoclinic
Space group	*Pbam*	$P2_1/c$		$P2_1/c$
a (Å)	17.6840(4)	9.7470(4)	9.691(12)	19.3879(14)
b (Å)	11.2190(8)	11.7365(4)	11.843(13)	11.8587(4)
c (Å)	10.957(4)	33.3202(11)	33.71(4)	19.7384(12)
α (°)	90	90	89.80(9)	90
β (°)	90	90.067(5)	89.43(10)	117.894(8)
γ (°)	90	90	89.73(10)	90
Volume (Å^3)	2173.8(8)	3811.7(2)	3869(10)	4010.9(5)
Z	2	4		4
ρ (calc. in Mg·m^{-3})	0.902	1.839		2.132
μ (mm^{-3})	0.330	8.180		11.481
F(000)	636	2040		2424
Crystal size (mm^3)	0.20 x 0.20 x 0.20	0.05 x 0.05 x 0.05		0.08 x 0.08 x 0.02
θ range for data collection (°)	2.303 – 32.470	2.422 – 31.867		2.335 – 32.435
Index ranges	$-26 \leq h \leq 22$,	$-7 \leq h \leq 13$,		$-29 \leq h \leq 29$,
	$-6 \leq k \leq 16$,	$-15 \leq k \leq 17$,		$-17 \leq k \leq 17$,
	$-15 \leq l \leq 15$	$-48 \leq l \leq 46$		$-29 \leq l \leq 29$
Reflections collected	19245	15991		16217
Independent reflections	3894 [R(int) = 0.0356]	9163 [R(int) = 0.0463]		16217 [R(int) = 0.1188]
Completeness (%) to 25.242°	99.90	99.90		99.90
Max. and min. transmission	1.00000 and 0.99209	1.00000 and 0.98835		1.00000 and 0.49178
Data / restraints / parameters	3894 / 0 / 83	9163 / 0 / 344		16217 / 0 / 347
GooF on F^2	0.989	1.055		0.963
Final R indices	R1 = 0.0401,	R1 = 0.0683,		R1 = 0.0629,
[I>2σ(I)]	wR2 = 0.0914	wR2 = 0.1368		wR2 = 0.1382
R indices (all data)	R1 = 0.0565,	R1 = 0.0857,		R1 = 0.1237,
	wR2 = 0.0986	wR2 = 0.1466		wR2 = 0.1482
Largest diff. peak and hole e·Å^{-3}	0.277 and –0.169	5.223 and –2.825		4.825 and –3.399

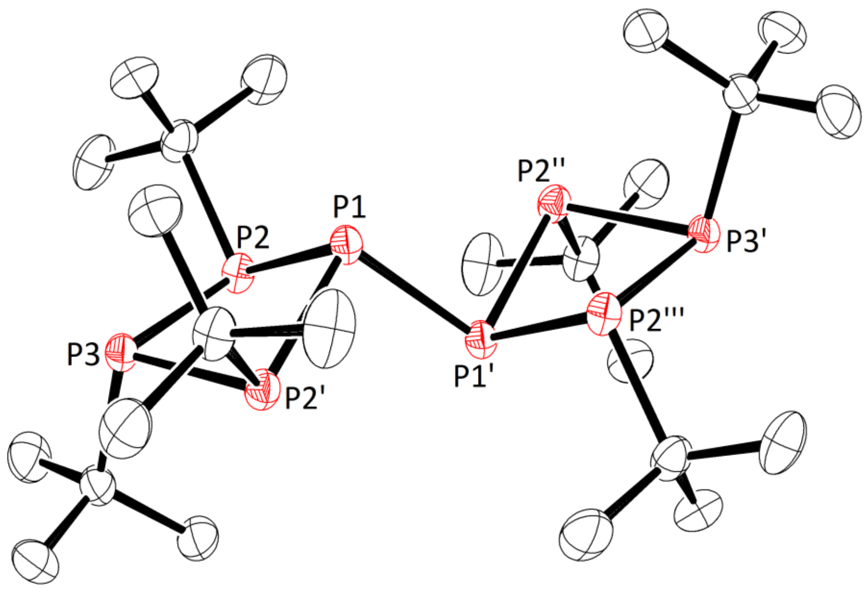


Figure S23. Molecular structure of phosphane **1**.

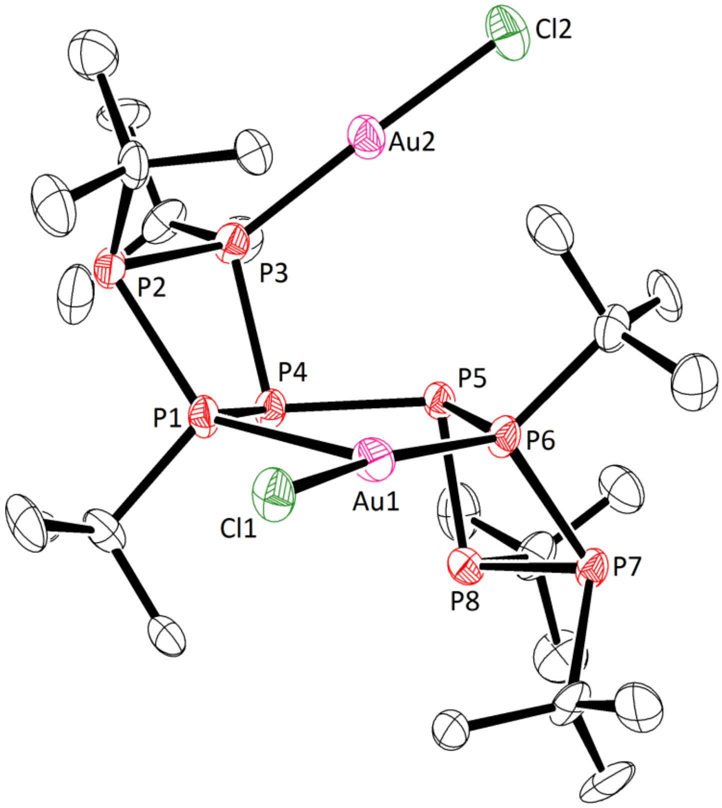


Figure S24. Molecular structure of homobimetallic complex **3**.

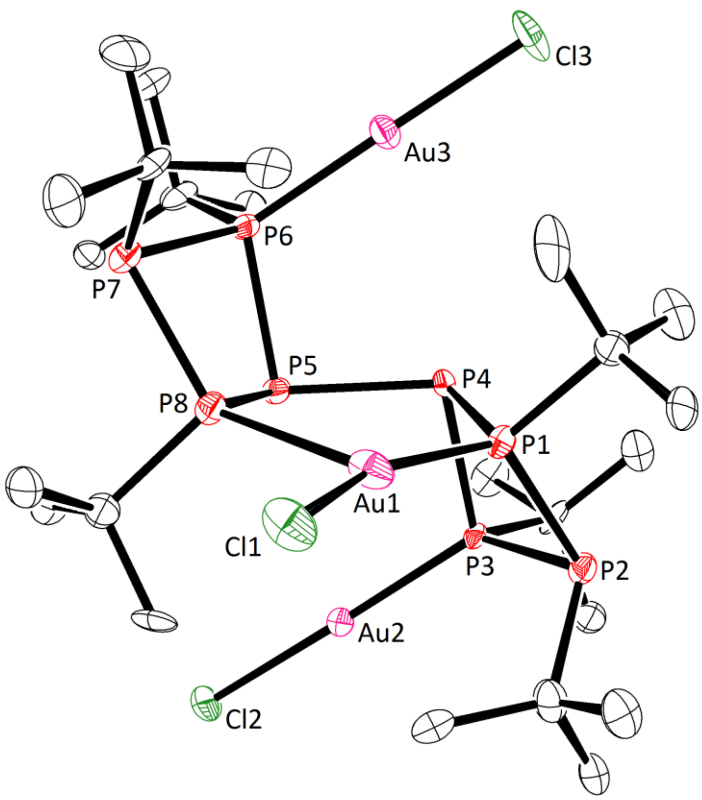


Figure S25. Molecular structure of homotrimetallic complex **4**.

Powder Measurements

Powder X-ray diffraction data were collected on a STADI-P diffractometer (STOE) with a silicon solid-state detector Methyn-1K (DECTRIS) at room temperature. The radiation source was a copper anode (Cu-K_α, λ = 1.540598 Å) combined with a germanium single crystal monochromator. Samples were measured in sealed glass capillaries (inner diameter 0.5 mm, HILGENBERG) with Debye-Scherrer geometry. Processing of the raw data was carried out with the diffractometer software WinXPow[12] (STOE). The theoretical powder pattern from the single crystal structures was calculated using MERCURY.[13]

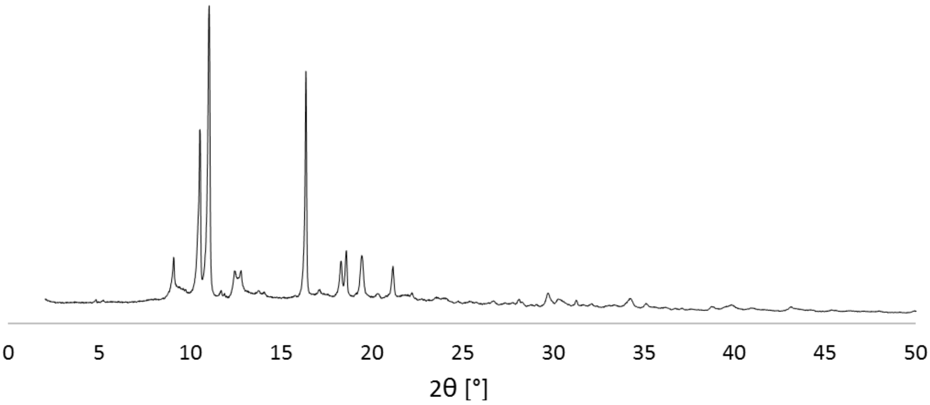


Figure S26. Powder X-ray diffraction pattern of **2**.

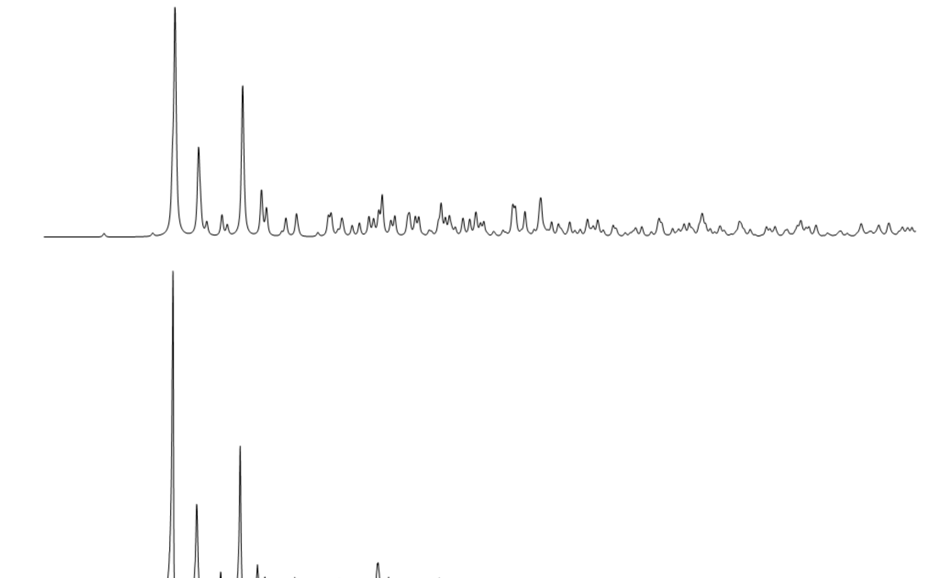


Figure S27. Calculated (top) and experimental (bottom) powder X-ray diffraction pattern of **3**.

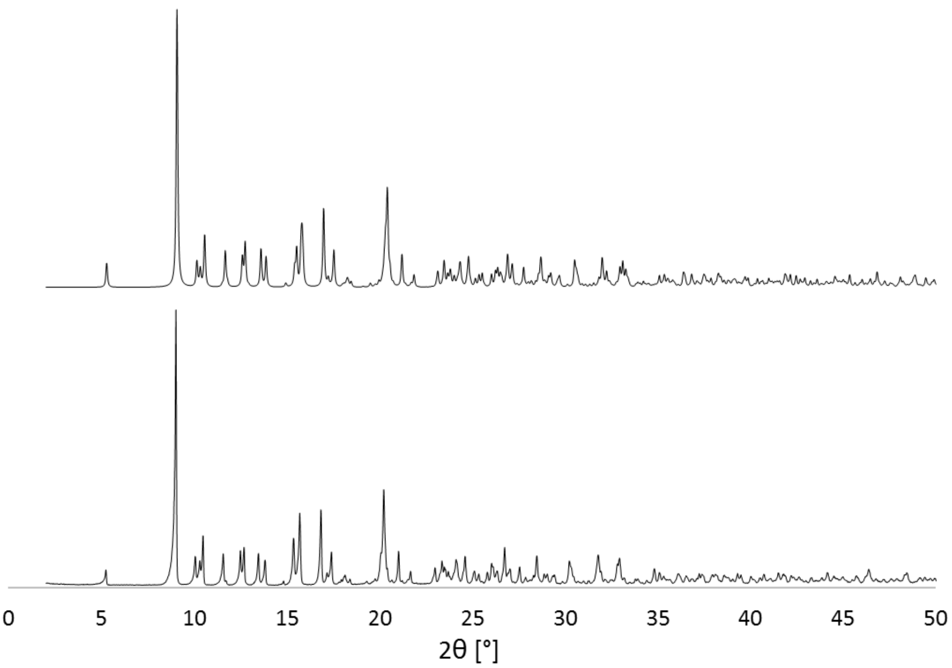


Figure S28. Calculated (top) and experimental (bottom) powder X-ray diffraction pattern of **4**.

CSD Search

The Cambridge structural database (CSD), version 5.39 (February 2018) was used for the crystal structure search. The searches have been performed using the program ConQuest, version 1.21.[14] The search motif was two phosphorus atoms connected to a gold atom allowing only three bonding atoms for the latter. Figure S29 shows the molecular structures for the search hits.

Table S2. Results of the CSD search. Structural formulas are given in Figure S29. L is the respective co-ligand. (a) This publication; (b) Observations in solution by $^{31}P\{^1H\}$ NMR spectroscopy; (c) Same observation made at –83 °C; (d) Same observation made at –90 °C; (e) Temperature of the single crystal XRD measurement in °C.

CSD Code	Au–P	Δ(Au–P)	P–Au–L	Δ(P–Au–L)	NMR[b]	Temp.[e]
CEXHAQ[15]	2.338(3) – 2.505(2)	0.167	121.9(3) – 156.6(3)	33.7	Equivalent	–173
CEXHIY[15]	2.3681(6) – 2.5311(5)	0.163	130.40(6) – 148.35(6)	18.0	Equivalent	–173
TIJLEF[16]	2.333(2) – 2.764(2)	0.431	127.7(2) – 154.5(2)	26.8	Equivalent[c]	–173
24[a]	2.240(3) – 2.673(3)	0.433	99.7(1) – 162.6(1)	62.87	Equivalent[d]	–143
25[a]	2.236(4) – 2.629(4)	0.393	105.5(1) – 156.4(2)	50.89	Equivalent[d]	–143

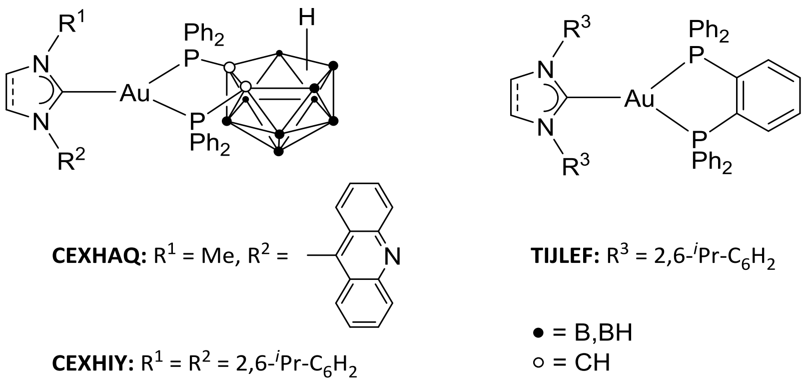


Figure S29. Molecular structures of the hits from the CSD search including their CSD code.

6. Quantum Chemical Calculations

General Remarks

All calculations were carried out with DFT using the program ORCA[17] (version 3.0.2). For all calculations, the convergence criterion was increased to 10^{-8} Hartree, the atom-pairwise dispersion correction D3[18] was used and, unless indicated otherwise, a simulation of the solvent environment was performed using the COSMO[19] model for which the dielectric constant was set to 7.58 (THF). Relativistic effects were considered using effective core potentials[20]. Furthermore, the RIJCOSX approximation was used to speed up the calculations. In all cases the free Gibbs energy ΔG was calculated using a numerical frequency analysis.

Benchmark Study

The method for optimizing the molecular structures of the gold(I) complexes was benchmarked based on the molecular structure of the trimetallic complex **4** obtained from single crystal XRD measurements. The BP86 functional[21,22] in combination with the def2-SVP[23,24] basis set was used due to the best agreement with the experimental data regarding the structural parameters shown in Table S3.

Table S3. Results from the benchmarking study to find the best functional and basis set combination structure for the geometry optimization of the gold(I) complexes. Experimental values taken from the molecular structure of complex **4**.

Method	Au–P	Au···P	Au–Cl	P–P
Experiment	2.236(4)	2.629(4)	2.322(5)	2.226(5)
BP86/def2-SVP	**2.281**	**2.625**	**2.386**	**2.237**
BP86/def2-TZVP	2.277	2.489	2.392	2.214
M06L/def2-TZVP	2.268	2.952	2.370	2.198
B3LYP/def2-TZVP	2.281	2.698	2.394	2.213
TPPSh/def2-TZVP	2.266	2.589	2.373	2.201
PBE0/def2-TZVP	2.274	2.586	2.373	2.196

Rotational Profile of 2,2',3,3',4,4'-Hexa-*tert*-butyl-1,1'-bicyclotetraphosphane {*cyclo*-(P_4tBu_3)}$_2$ (1)

These calculations were carried out using the B3LYP functional in combination with the def2-TZVP[23,24] basis set. To obtain the rotational profile of the dihedral angle τ was varied in steps of 5°. The complex was subsequently optimized, restraining the dihedral angle τ. A frequency analysis was carried out to obtain the ΔG values.

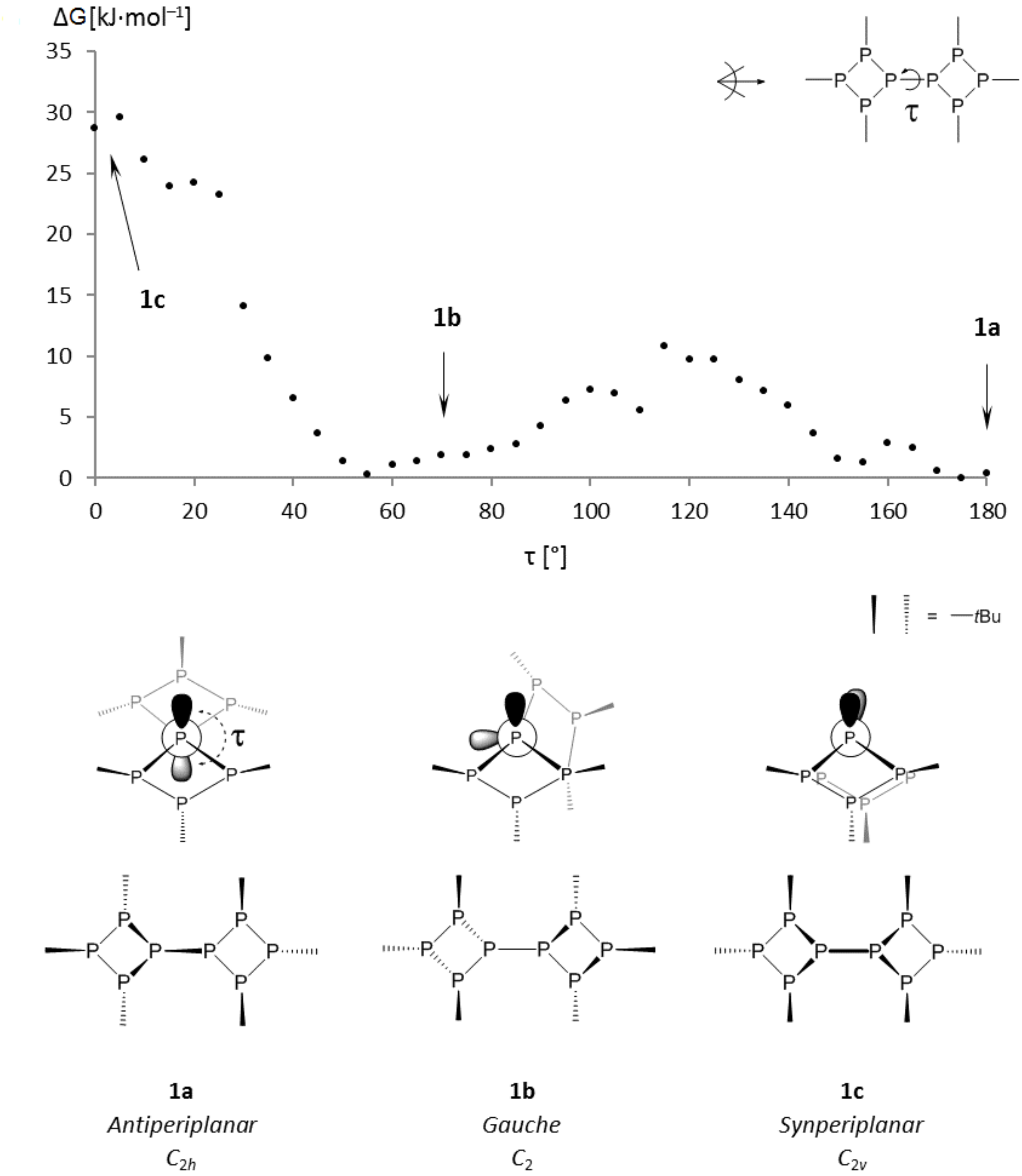


Figure S30. Rotational profile of phosphane **1**.

Table S4. Individual energy values [kJ·mol⁻¹] with dihedral angles τ [°] for the rotational profile of phosphane **1**.

τ	ΔG_{rel}	τ	ΔG_{rel}	τ	ΔG_{rel}	τ	ΔG_{rel}	τ	ΔG_{rel}	τ	ΔG_{el}
0	28.0	35	10.5	70	1.0	105	9.6	140	8.0	175	1.0
5	29.5	40	7.0	75	1.1	110	8.4	145	5.0	180	1.4
10	26.2	45	3.8	80	2.3	115	13.7	150	3.7		
15	23.9	50	1.2	85	3.4	120	12.5	155	3.2		
20	23.8	55	0.0	90	5.2	125	12.2	160	4.4		
25	23.3	60	0.4	95	7.5	130	10.6	165	3.5		
30	14.6	65	0.6	100	9.7	135	9.5	170	1.5		

Rotational Profile of [AuCl(1)] (2)

To obtain the rotational profile of the monometallic gold(I) complex **2**, the angle τ' (Figure S31) was varied in steps of 5°. The complex was subsequently optimized, restraining the dihedral angle which corresponded to the P atom that was attached to the Au–Cl fragment. The individual values are listed in Table S5. In addition to the BP86/def2-SVP, different levels of theory were tested but showed no significant difference.

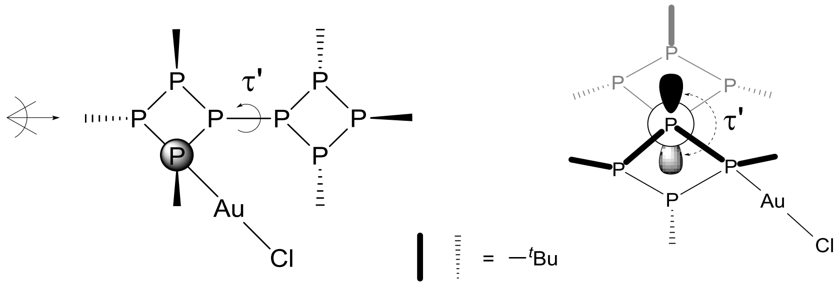


Figure S31. Definition of dihedral angle τ' in complex **2**.

Table S5. Individual energy values (kJ·mol^{-1}) with dihedral angles τ'(°) for the rotational profile of complex **2**.

τ'	ΔG_{rel}	τ'	ΔG_{rel}	τ'	ΔG_{rel}
0	21.8	120	37.8	240	15.7
4	17.0	124	38.3	244	10.7
8	11.2	128	26.1	248	12.4
12	12.0	132	27.3	252	14.2
16	10.8	136	21.7	256	7.6
20	10.1	140	25.9	260	5.2
24	8.1	144	24.9	264	4.7
28	9.8	148	23.6	268	3.2
32	10.4	152	17.4	272	1.5
36	15.6	156	16.1	276	0.0
40	11.4	160	16.6	280	0.9
44	18.2	164	15.9	284	3.3
48	28.5	168	21.5	288	7.7
52	26.3	172	22.8	292	9.9
56	30.2	176	23.8	296	18.3
57	30.9	180	24.8	300	17.8
58	31.6	184	27.9	304	26.9
59	32.3	188	30.8	308	29.3
60	38.5	192	36.0	312	29.8
64	39.6	196	38.5	313	30.5
68	38.8	200	43.2	314	32.0
72	38.5	204	48.0	315	34.1
76	35.2	208	51.5	316	34.0
80	34.8	209	51.8	317	36.5
84	32.5	210	53.0	318	42.4
88	36.0	211	53.6	319	43.5
92	36.2	212	53.7	320	37.6
96	33.2	213	39.3	324	28.2
97	33.4	214	38.5	328	28.2
98	31.3	215	37.9	332	22.3
99	31.8	216	37.2	336	16.6
100	49.1	220	33.5	340	16.4
104	54.0	224	29.3	344	15.9
108	47.6	228	27.7	348	21.5
112	44.2	232	23.6	352	17.3
116	39.1	236	18.8	356	16.6

Rotational Profile of [(AuCl)₂(1)] (3)

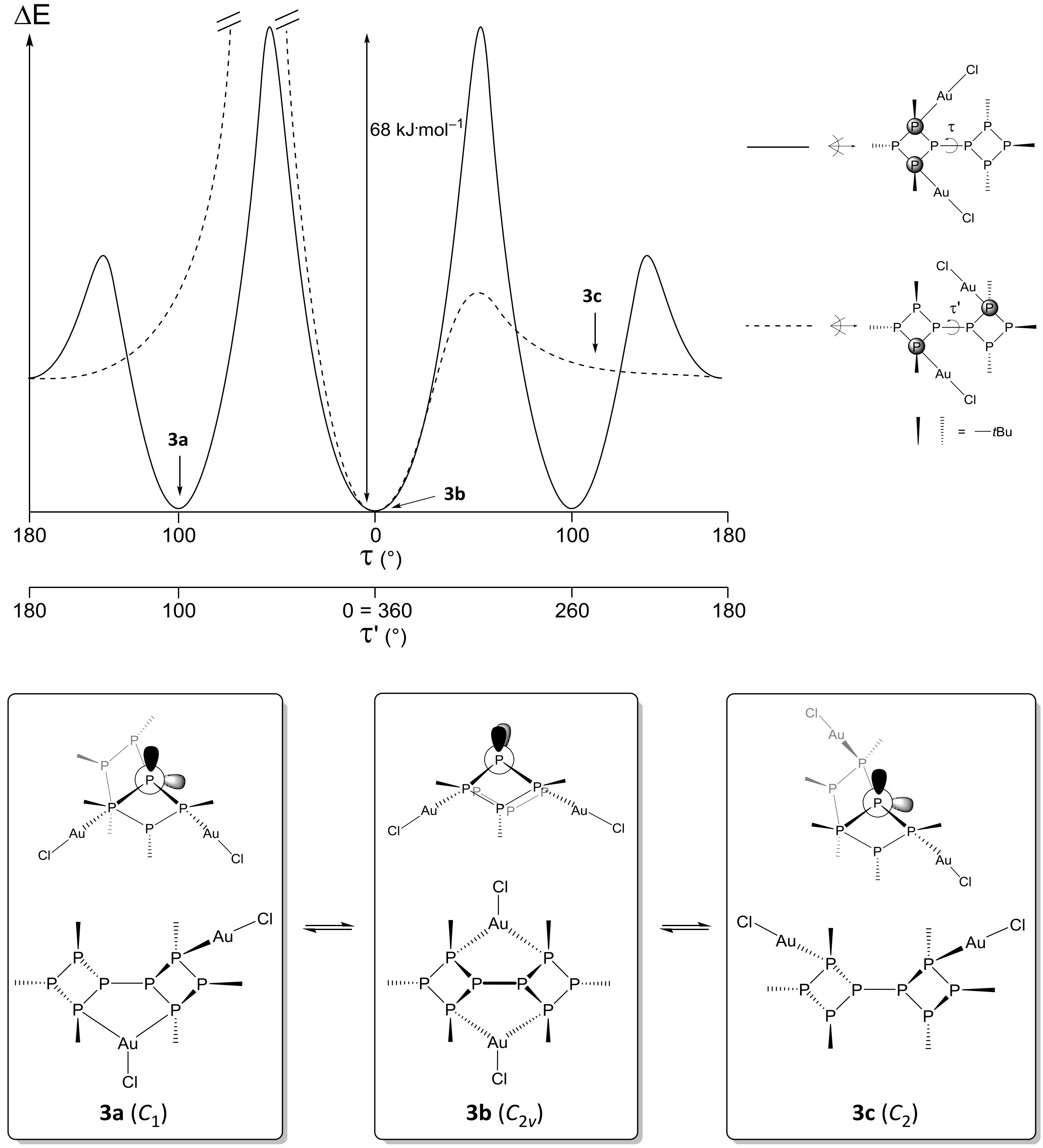


Figure S32. Illustration of the dynamic process in the bimetallic complex **3. Top**: Estimated rotational profile; **Bottom**: Involved conformers with corresponding molecular symmetry indicated in brackets.

In the rotational profile of complex **3**, the barriers that arise from the steric repulsion between the bulky ^{t}Bu groups and the Au–Cl fragments and cleavage of the favored distorted T-shaped chelation are +29.1 and +39.1 kJ·mol^{-1} (corresponding activation energies to transform **3a** into **3b** and **3c**, respectively). As bimetallic complex **3** possesses two Au–Cl fragments, rotational barriers of approximately +68 kJ·mol^{-1} are expected at certain angles τ and τ' for a rotation around the internal P–P bond. In this way, the rotational profile of **3** as shown in Figure S32 can be estimated. It should be noted that two mutually connected rotational profiles are possible. Both cases are discussed in the following:

- If both Au–Cl fragments are coordinated by the same P_4 ring, a symmetrical profile with a range of 180° (represented by τ, solid line in Figure S32) results. Two minima are expected corresponding to a *synperiplanar* conformation **3b** (τ ≈ 0°) and a *gauche* conformation **3a** (τ ≈ 100°) which should be separated by a barrier of about +68 kJ·mol^{-1}. DFT calculations reveal that both rotamers are almost isoenergetic (ΔG(**3b**–**3a**) = –0.4 kJ·mol^{-1}). A low activation barrier is expected for the rotation which transforms **3a** (C_1 symmetry) into its enantiomer (τ ≈ 100°). In this range, an additional rotamer with *antiperiplanar* conformation, featuring two linearly coordinated Au–Cl fragments, is conceivable.

- If each P_4 ring coordinates a gold(I) atom, an asymmetrical profile results which covers 360° (represented by τ', dashed line in Figure S32). This profile is expected to feature an extremely high rotational barrier due the repulsion of the Au–Cl groups at τ = τ ' ≈ 100°. The minimum at τ ' ≈ 0° corresponds to a *synperiplanar* rotamer. This should directly be connected to rotamer **3b** by a single Y-shape interconversion rendering this a crossing point between the two systems (with an equally low activation barrier). In addition, at least one minimum which corresponds to an *antiperiplanar* conformer **3c** with two linearly coordinated gold(I) atoms is conceivable.

The assignment to the conformers of **3** to the $^{31}P\{^1H\}$ NMR spectrum is not entirely clear. The Y-shape coordination flip should lead to three signals with a relative intensity of 2:1:1 for the conformer with *synperiplanar* conformation (**3b**) which would match with the second signal set. The first signal set would accordingly correspond to the *gauche* rotamer **3a**. However, for this conformer either eight signals are expected or three signals with a relative intensity of 2:1:1 considering a rotation around the internal P–P bond leading, similarly to **2**, to a dynamic process which makes all β-P atoms equivalent. Unfortunately, all attempts to elucidate this behavior by further NMR studies were impeded by the low solubility of the complex.

Molecular Orbital Energies

These calculations were carried out using the BP86[21,22] functional in combination with the def2-SVP[23,24] basis set.

Table S6. Molecular orbital energies of the molecules **1**-**4**.

{*cyclo*-(P_4tBu$_3$)}$_2$ (**1**)		[AuCl(**1**)] (**2**)		[(AuCl)$_2$(**1**)] (**3**)		[(AuCl)$_3$(**1**)] (**4**)	
Orbital	**Energy [eV]**	**Orbital**	**Energy [eV]**	**Orbital**	**Energy [eV]**	**Orbital**	**Energy [eV]**
HOMO	–5.098	HOMO	–4.696	HOMO	–4.876	HOMO	–5.109
HOMO–1	–5.219	HOMO–1	–5.497	HOMO–1	–5.659	HOMO–1	–6.108
HOMO–2	–5.244	HOMO–2	–5.593	HOMO–2	–5.996	HOMO–2	–6.124
HOMO–3	–5.416	HOMO–3	–5.887	HOMO–5	–6.196	HOMO–3	–6.272
HOMO–4	–5.581	HOMO–4	–5.949	HOMO–7	–6.468	HOMO–9	–6.616
HOMO–5	–6.021	HOMO–6	–6.185	HOMO–8	–6.599	HOMO–10	–6.728
		HOMO–7	–6.511	HOMO–10	–6.866		

Transition States

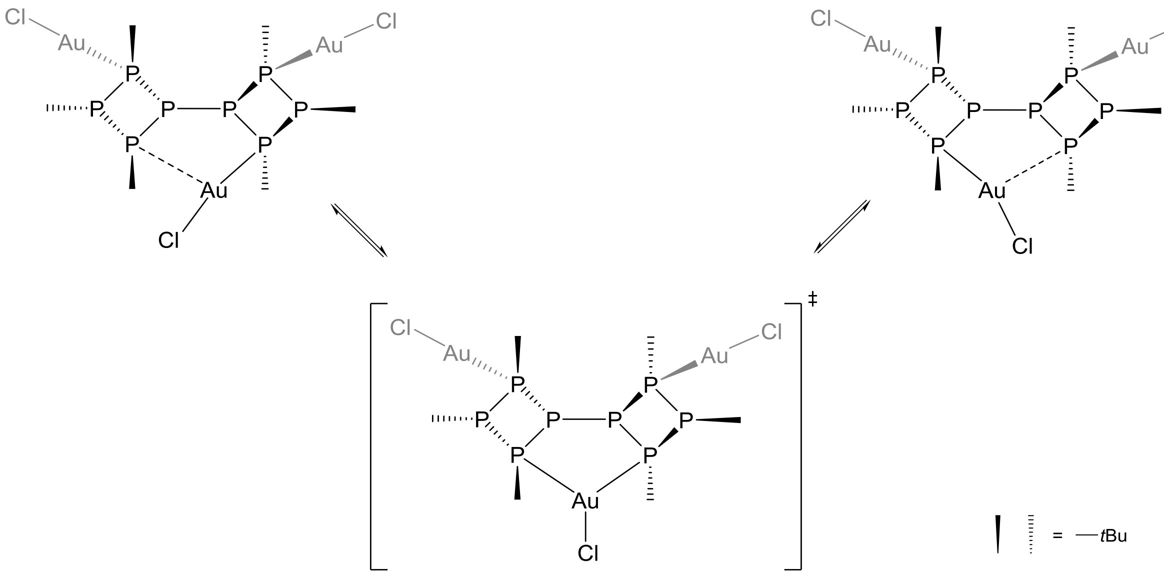


Figure S33. Representation of the Y-shape coordination flip of the chelated gold(I) atom in complexes **2**-**4**.

These calculations were carried out using the BP86[21,22] functional in combination with the def2-SVP[23,24] basis set according to the results of the benchmark study. The transition states for the Y-shape coordination flip were located by a relaxed surface scan of the P–Au–Cl bond angle using the method described above. The transition state structures were verified as such by showing only one negative eigenvalue of the Hesse matrix which corresponds to the described chemical motion. Furthermore, these structures were moved along the respective mode and subsequently optimized which yielded the two corresponding minima.

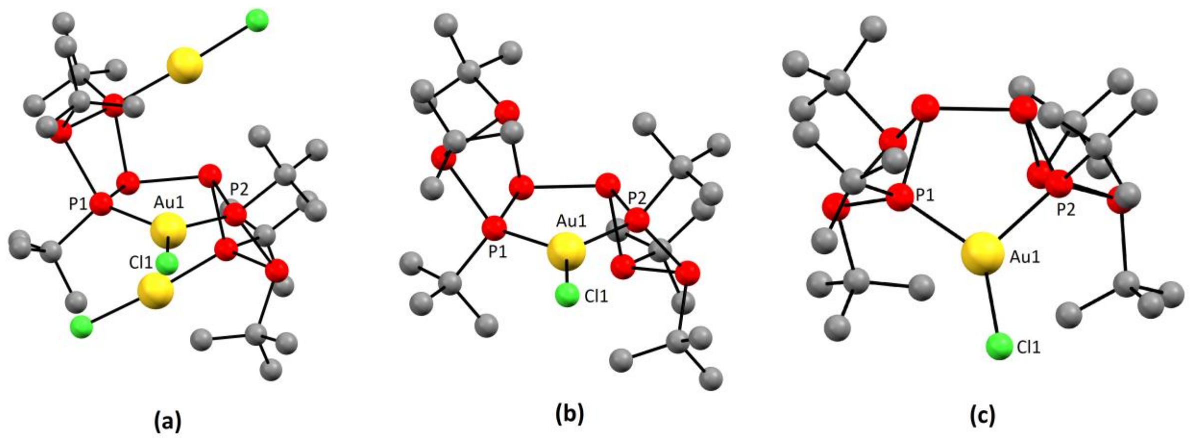


Figure S34. Calculated transition states for the Y-shape coordination flip of gold(I). Homotrimetallic complex **4** with *gauche* conformation (a), monometallic complexes **2a** with *gauche* conformation (b) as well as **2b** with *synperiplanar* conformation (c). Structural parameters given in Table S7.

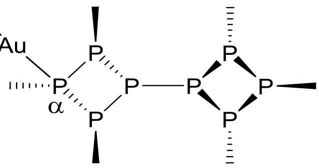
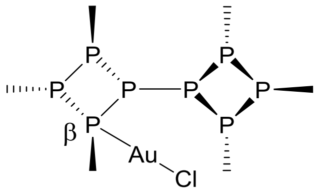
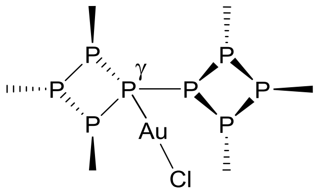
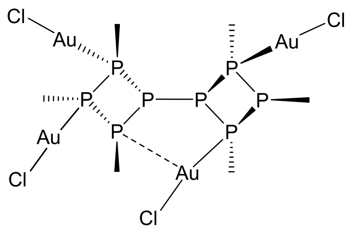
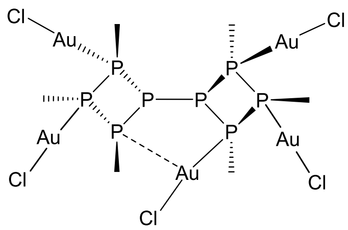
Table S7. Activation energies ΔG [kJ·mol^{-1}] as well as selected bond lengths [Å] and angles [°] of the calculated transition states of complexes **2** and **4**. Letters in brackets correspond to the transition state structures in Figure S34.

Parameter	**Complex 4 (a)**	**Complex 2 (b)**	**Complex 2 (c)**
Conformation	*gauche*	*Gauche*	*Synperiplanar*
G_{act}	+10.0	+13.7	+17.6
Au(1)–P(1)	2.3915	2.3918	2.3732
Au(1)–P(2)	2.3806	2.3918	2.4217
P(1)–Au(1)–P(2)	100.08	99.82	99.05
Cl(1)–Au(1)–P(1)	128.83	129.96	136.2
Cl(1)–Au(1)–P(2)	131.09	130.22	124.33

Complex Formation Energies

These calculations were carried out using the BP86[21,22] functional in combination with the def2-TZVP[23,24] basis set.

Table S8. Complex formation energies of hypothetical monodentate complexes as well as complexes with up to five Au–Cl fragments. ΔΔG refers to the complex formation energy with one Au–Cl fragments fewer.

Reaction	ΔG_{react} [kJ·mol^{-1}]	ΔΔG [kJ·mol^{-1}]
1 + [AuCl(tht)] → (- tht) 	–87.3	
1 + [AuCl(tht)] → (- tht) 	–100.4	
1 + [AuCl(tht)] → (- tht) 	–82.3	
P_8tBu_6 (**1**) + [AuCl(tht)] → (- tht) [(AuCl)(P_8tBu_6)] (**2**)	–119.8	
[(AuCl)(P_8tBu_6)] (**2**) + [AuCl(tht)] → (- tht) [$(AuCl)_2$(P_8tBu_6)] (**3**)	–204.3	–84.5
[$(AuCl)_2$(P_8tBu_6)] (**3**) + [AuCl(tht)] → (- tht) [$(AuCl)_3$(P_8tBu_6)] (**4**)	–296.6	–92.2
[$(AuCl)_3$(P_8tBu_6)] (**4**) + [AuCl(tht)] → (- tht)  [$(AuCl)_4$(P_8tBu_6)]	–365.5	–59.9
[$(AuCl)_4$(P_8tBu_6)] + [AuCl(tht)] → (- tht)  [$(AuCl)_5$(P_8tBu_6)]	–406.0	–49.5
 = —tBu		

Cartesian Coordinates from Geometry Optimizations of Selected Molecules

Table S9. Cartesian coordinates of optimized structures for the conformers of complex **2**.

Rotamer 2a				Rotamer 2b				Rotamer 2c			
P	0.17401128028648	-0.16947954910993	-0.12325557835051	P	-0.04757615414377	-0.26276762336931	-0.11390712834349	P	0.12124176635390	0.29063998556102	-0.29781244801520
P	-0.02837929080140	-0.02693515477206	2.12540817602776	P	-0.20232384670023	0.00506603727223	2.14067332741589	P	0.11658960115917	0.04828377290277	1.95900161316365
P	2.19887370570073	0.11058231897997	2.10277973075011	P	2.02211739181059	-0.06338670436092	2.00036853574809	P	2.29667688062546	0.49970352293338	1.85931938997602
P	2.04352795956685	1.08412383318717	0.08004885647893	P	1.80871815868149	1.02425699697853	0.05695772071923	P	2.06156788338641	1.45024421695717	-0.15724104150251
P	3.28842853193198	-0.00338684423770	-1.39308263102793	P	3.36603755234703	0.17799781561661	-1.35713670898548	P	3.19986470127344	-0.20059486227292	-1.15484924518926
P	5.24154810113938	1.07623566606937	-1.08156023844308	P	3.86303667097320	-1.89019529098568	-0.64383409338174	P	2.31231003384638	0.32006920925403	-3.16470491032876
P	6.22429798167850	-0.95757165337922	-1.20524410213322	P	3.34687747583155	-2.66555910115098	-2.69067003652155	P	4.42252917256635	0.80077241208637	-3.81712937511381
P	4.28765016738294	-1.72196226247250	-0.36293183291711	P	2.02439870505209	-0.84403771812616	-2.86173312739108	P	4.96242105180946	1.12860815372461	-1.65328475910913
C	3.80895937748177	-3.23476025133374	-1.41222046440150	C	2.62724093377566	-0.06930366588544	-4.50837533032590	C	6.48667209467900	0.00633128735490	-1.38779034035787
C	5.53607842349110	1.81398651913050	-2.82360513525499	C	5.77255510639835	-1.90164717881591	-0.61080753757315	C	2.01372093651444	-1.40116387553146	-3.94755538886034
C	7.37781879738544	-0.99025758758376	0.32589159361663	C	2.11015432775345	-4.06069123783649	-2.25466413781334	C	4.21704728464898	2.60363030607584	-4.43659996781911
C	-1.07455387415572	1.13540456847833	-0.76038739432218	C	-1.32454656470209	1.01924200567067	-0.75962396266955	C	-1.17502545406685	1.66971262377521	-0.56129536150561
C	-0.44392636357353	-1.81201708212975	2.68765270851033	C	-0.76201535150333	-1.70154385933412	2.82290950003690	C	-0.00595415842489	-1.85130913413754	2.18206106825839
C	2.71367804450592	1.49319477571849	3.28959547031893	C	2.79715541895183	1.17013189538023	3.20680058352305	C	2.71059580450706	1.82566534117913	3.12877240836275
Au	3.49648428350428	-1.77321276192456	2.15033114548854	Au	3.02043971558794	-2.11600170555428	1.87960496138602	Au	3.80129262484170	-1.20981541374753	1.82398378108913
Cl	4.58792916194996	-3.76673959125656	2.91928954155516	Cl	3.86455585828286	-4.28427093007742	2.43340472650199	Cl	5.34870357578912	-2.96619134243560	1.87590941348556
C	6.99389875674856	2.30708521540997	-2.82098247431800	C	6.19239946285485	-1.07887315681378	0.61731003659058	C	1.83193127258413	-1.13152985977687	-5.45222566565572
C	5.30704967835188	0.82015166365303	-3.96882918497163	C	6.15600786638238	-3.38304499927455	-0.44386621916345	C	3.16179626448276	-2.38984558554576	-3.71276477843325
C	4.55066304291940	2.99333243826680	-2.92362852774763	C	6.40023385953534	-1.31862657368206	-1.88277249896178	C	0.71386923851116	-1.93457874118815	-3.32153214458903
H	7.70365902771444	1.45905944556104	-2.72068781135637	H	7.29923396164771	-1.08111317277283	0.71175498726002	H	2.76159557103080	-0.72448123723498	-5.90316390411248
H	7.22307540301817	2.82305258280995	-3.77818094649862	H	5.86474844436589	-0.02257018002565	0.52412506886440	H	1.58950952820779	-2.07869725251328	-5.98051029480394
H	7.18673089756468	3.02108039201734	-1.99349187544818	H	5.76658137315850	-1.49632080519360	1.55338443384501	H	1.00805128610340	-0.41315246304959	-5.64425586316406
H	5.48609397039198	1.32056708155605	-4.94525057605163	H	5.69809693709355	-3.82483708652009	0.46529299379785	H	2.92475309346772	-3.36631731508075	-4.18869949772798
H	5.99535214920607	-0.04602827998096	-3.89444396756562	H	5.83745008098873	-3.97976720579762	-1.32409165094370	H	4.11085358685158	-2.01792135315109	-4.14886535542242
H	4.26657267143773	0.43495359600256	-3.97005265862329	H	7.26071137187822	-3.47298464226568	-0.36226096079832	H	3.32473403821398	-2.57122490537266	-2.63038384520665
H	4.69049310433641	3.52582125428508	-3.88892587974604	H	7.50835224514376	-1.37183742313548	-1.81039848474318	H	0.45698778254710	-2.91908293636462	-3.76861585108777
H	3.49747905227370	2.64151510085285	-2.88507514349538	H	6.08768953741205	-1.88487910488640	-2.78297046368992	H	0.82030591812780	-2.07037293131082	-2.22575205290085
H	4.69945419484935	3.72486946998066	-2.10263918057708	H	6.11772019427009	-0.25567254514543	-2.02443752992239	H	-0.13750040383880	-1.24393075610618	-3.49036426305980
C	2.53865895346960	0.94081401297090	4.71370082537256	C	2.80392842855984	0.51022849505653	4.59507332037856	C	2.65348084360063	1.14857830169449	4.50811670210259
C	4.19082304174158	1.78200899678256	2.97929624458793	C	4.22921083561920	1.39554155880233	2.69463771981274	C	4.13525252200118	2.29564150498771	2.78353219570008
C	1.84720231727325	2.74162078131798	3.07235950821734	C	1.99841256398840	2.48028280185051	3.21879663596857	C	1.70615989263008	2.98191015936303	3.02999835452462
H	2.87781692547436	1.70038111791812	5.44940651617348	H	3.31363992320678	1.17980902590579	5.31945308394475	H	2.92316270926627	1.88320513847392	5.29564346335948
H	1.47582641117918	0.71034513595771	4.93182777080515	H	1.77430284411965	0.33248142895282	4.96462159124338	H	1.63378390264720	0.77157452956996	4.73130638602853
H	3.13493188774265	0.01795234620378	4.86520736929424	H	3.34122611718415	-0.46022032453395	4.57970155627022	H	3.36268979842538	0.29757248680735	4.57155006652184
H	4.54522139683963	2.62655650624915	3.60675866205016	H	4.75046454726710	2.12173500078143	3.35301059650725	H	4.43731166211899	3.10747744598652	3.47785920126514
H	4.82432374976913	0.90000424990492	3.19619959267311	H	4.80920440986329	0.45171985460663	2.69369153555671	H	4.86842851581490	1.46860750001625	2.87551311111392
H	4.34213857747150	2.06079677801751	1.91432142081143	H	4.23355386445356	1.81145965786382	1.66453312867392	H	4.19284186483242	2.69433189665197	1.74845942244478
H	2.15464871897757	3.53076310473492	3.79075047157096	H	2.47698293251832	3.19628425020289	3.91996102211995	H	1.96469645287068	3.76119228551137	3.77735756690498
H	1.96728001700653	3.14729076770323	2.04728852818425	H	1.97164356172422	2.94781095350982	2.21352482345543	H	1.72667393335542	3.45341092458131	2.02640190032233
H	0.77252068793855	2.52483681786332	3.23780875678348	H	0.95376443273233	2.31510295152320	3.55073026364499	H	0.67201085306435	2.63934935382598	3.23523935651723
C	0.02940321087015	-1.92008313547597	4.14694308059790	C	-0.12894258526584	-1.84322981853931	4.21688236111544	C	0.59105975916474	-2.16314071596637	3.56493704022568
C	-1.98177046512267	-1.87829069064452	2.60092205269052	C	-2.29413612058763	-1.56296385369196	2.93477911853326	C	-1.52416924187709	-2.12251890955961	2.16390567820822
C	0.18042776557327	-2.91698108548830	1.83364613424885	C	-0.40362529501184	-2.89825180683070	1.94187714906502	C	0.68331048513174	-2.67399857010850	1.08717373717545
H	-0.29598999893504	-2.89315746087589	4.57262516327927	H	-0.53390406664636	-2.74735063879039	4.71948809271112	H	0.42457113713398	-3.23336618489856	3.81115959705699
H	1.13699397076286	-1.87952616563471	4.21129575222652	H	0.97208232399553	-1.96576655810361	4.14521600928967	H	1.68780626569407	-1.98600653175751	3.58031893350842
H	-0.39241445045658	-1.11293822097771	4.78131477454049	H	-0.34868035937063	-0.96864260270987	4.86424898498277	H	0.12456010947071	-1.55191027750801	4.36522785979463
H	-0.12104678231736	-3.91201590530537	2.22526498499282	H	-0.78997938020498	-3.83253243186715	2.40295480804150	H	0.56619262958475	-3.75689605155936	1.30607900071589
H	-0.13716162400220	-2.84663927176825	0.77481764153877	H	-0.83345183346680	-2.80661010956647	0.92526577511643	H	0.24557679338462	-2.47118684118904	0.09002412623515
H	1.29050103925766	-2.86802905080653	1.86342492699187	H	0.69742291460109	-3.00729794138632	1.83841244783039	H	1.77213116266507	-2.45812617181486	1.02912485634288
H	-2.33394056898078	-2.86264253728689	2.97672782960155	H	-2.71907853850266	-2.48317170342686	3.38945107444516	H	-1.71050885033752	-3.20617023773509	2.32197861754066
H	-2.46602130939651	-1.08564708849856	3.20781138214872	H	-2.58745127940835	-0.69978777857180	3.56705256831794	H	-2.05508843749170	-1.56218297184612	2.96057860550432
H	-2.33277216807778	-1.77890613492897	1.55256327345941	H	-2.76401790343577	-1.43848314524905	1.93712306295556	H	-1.97243870324067	-1.84845910004945	1.18561269035283
C	-2.45863357688895	0.46866261294043	-0.67118385775531	C	-2.68709515035175	0.30857603790808	-0.66812603326976	C	-2.53493908781532	1.00106197029751	-0.29005780311179
C	-1.05963006186780	2.45230131400318	0.02445221421273	C	-1.35131761269070	2.33884794292437	0.01966550607905	C	-0.98359909203763	2.88976393429946	0.34672523629831
C	-0.66903303911795	1.37411453528783	-2.22735250981883	C	-0.94202159411176	1.27584321763515	-2.22690576730016	C	-1.04054708075440	2.07187763279638	-2.04137387917093
H	-1.79418464675834	3.16152653665770	-0.41487157465046	H	-2.09663154608237	3.02802534744625	-0.43372542306994	H	-1.77338586877537	3.64384860970322	0.13864862410392
H	-1.32921072321562	2.29311883022376	1.08813519840347	H	-1.63014509356095	2.18001322169590	1.08070112105065	H	-1.05046837455277	2.61325473638356	1.41817265591688
H	-0.06025939763610	2.93270153014291	-0.00932627856545	H	-0.36275094109102	2.84190407481499	-0.00334780440090	H	-0.00121038630575	3.37437288942618	0.17114406276410
H	-3.22858551905987	1.13083198880405	-1.12227646025013	H	-3.47892943593301	0.94685910002268	-1.11588131891261	H	-3.35804006955115	1.71637804756067	-0.50309837891188
H	-2.48588077241559	-0.50174481883793	-1.20888363129466	H	-2.68449648346978	-0.66129397377281	-1.20746358880216	H	-2.68780713086184	0.10550624652671	-0.92735367516776
H	-2.75172293185238	0.29037740563619	0.38456877856369	H	-2.97365961118744	0.11834230102733	0.38721288732196	H	-2.62871761301860	0.69372884062157	0.77309534592083
H	-1.38386868956805	2.07515618422952	-2.70919195534064	H	-1.69658079035187	1.93679471298270	-2.70534052212495	H	-1.80327992534591	2.83966470166299	-2.29337803633507
H	0.34269423782281	1.82759492896492	-2.29689897574511	H	0.04150667686128	1.78514113435098	-2.29790449848546	H	-0.03910922694555	2.49980162809351	-2.25524155181491
H	-0.66414627832080	0.43166370045572	-2.81297800427856	H	-0.87943300533482	0.33516973939762	-2.81044595693386	H	-1.18383104312898	1.20504183707637	-2.71804633061690
C	7.61723945108370	-2.47638550775077	0.64599522405822	C	1.48787993347338	-4.48283810439335	-3.59753629867147	C	5.64440258471041	3.16140639212711	-4.57368982532279
C	8.67526435444354	-0.30849029841084	-0.14867980778055	C	2.95890761742282	-5.19339906875843	-1.64862065057849	C	3.53117933193199	2.49141300840383	-5.80957783561116
C	6.81766905815212	-0.26815145290703	1.55398416137937	C	1.02370130669863	-3.63714133326903	-1.26375315020143	C	3.38539473611789	3.48673837495242	-3.49574854995531
H	9.43184081224407	-0.32857335945741	0.66499826858521	H	2.32158918265641	-6.08922112481512	-1.48506343307139	H	3.41801260681044	3.49981319895012	-6.26305185163353
H	9.10993250589180	-0.81763811384950	-1.03372974455128	H	3.79677546246465	-5.49037003410924	-2.31349786067229	H	4.11668406830675	1.86347818883208	-6.51274450990750
H	8.49866951673946	0.75565675076701	-0.41263813363972	H	3.37461622800279	-4.90020208447280	-0.66134382731661	H	2.51516828608193	2.05253073234255	-5.71541240887628
H	8.40392683863602	-2.56518153211629	1.42611112124555	H	0.78832313884363	-5.33204044348837	-3.44073700843647	H	5.61220699558065	4.19453613534734	-4.98211964506127
H	6.70087537512396	-2.95717550900126	1.04801811351381	H	0.90618952576590	-3.65140680552300	-4.04915174565468	H	6.15325995426719	3.20829291706240	-3.58761022072608
H	7.95998133420183	-3.04330611587921	-0.24491417405073	H	2.25888878314370	-4.80390760760616	-4.32839232569682	H	6.26513041212526	2.54285127993828	-5.25456062479921
H	7.53234536567938	-0.34986511402279	2.40131333837620	H	0.35617378789282	-4.49719616779472	-1.03886509847028	H	3.30971532418465	4.51608791816299	-3.90937430292910
H	6.64050474584325	0.80624875850179	1.35060229226325	H	1.47055785646812	-3.29744052952942	-0.30883352356993	H	2.35721754091251	3.08817443404849	-3.37481151322870
H	5.85634944104508	-0.71840034818017	1.88073827251509	H	0.40539773533225	-2.80377794931755	-1.65180725612197	H	3.84667103549991	3.55274159042078	-2.48918232238774
C	2.34479874872617	-3.53460382325558	-1.05159408142962	C	2.03736437315283	1.35121444015944	-4.54674837396211	C	6.85069610723574	0.18537945587591	0.09785461961547
C	3.96538759017660	-2.98509545868581	-2.91696759272338	C	4.15224007061632	-0.01605963038454	-4.65951454711346	C	6.23296111425539	-1.46950817096006	-1.71380162356043
C	4.73692369951211	-4.36764009926698	-0.93781593692602	C	2.00862914437543	-0.95352013477645	-5.60665803233905	C	7.59228324959602	0.57958824406854	-2.29190091957181
H	1.98022251349720	-4.39948115180802	-1.64580416478151	H	2.33682300018318	1.86016401421453	-5.48807458600624	H	7.72632632238259	-0.44704659239711	0.35732485090047
H	2.24069101537205	-3.78749441683572	0.02171852290436	H	0.93015508302506	1.33875965090621	-4.50379878611446	H	7.09876754574842	1.24095682096062	0.33195919708056
H	1.68166224223652	-2.66902946701599	-1.26595369336404	H	2.41247576440457	1.96719883456877	-3.70145428915595	H	6.01445968355760	-0.12991896625500	0.75809757852579
H	3.70161004923999	-3.90753245972587	-3.47870548903054	H	4.41822427630931	0.42394440724711	-5.64533813047451	H	7.16103647538755	-2.05837717514173	-1.54688663159338
H	3.29778112612510	-2.17005419723985	-3.26395005145707	H	4.61367394031065	0.61189521351111	-3.87066385499362	H	5.44810581047420	-1.90075414240716	-1.06018582567329
H	5.00861774560511	-2.71117753398405	-3.17461523440416	H	4.59967679626403	-1.02873957381478	-4.60363764270163	H	5.92942603850826	-1.60051849003996	-2.77183954022912
H	5.79491828531257	-4.15523934587900	-1.19577278450192	H	2.24569075668691	-0.53527985970299	-6.60850440750264	H	8.54256829062648	0.03050096484809	-2.11768111526217
H	4.66828615430843	-4.51745653845448	0.15989176322495	H	2.41782035492363	-1.98521843987683	-5.56941751510698	H	7.33105998158944	0.47182166313022	-3.36577323408073
H	4.45233188933692	-5.31657924487172	-1.44104341526244	H	0.90424639782699	-1.01362163110433	-5.51415999166110	H	7.77950736749323	1.65410531281912	-2.08474480542399

Table S10. Cartesian coordinates of optimized structures for the conformers for complexes **3** and **4**.

Rotamer 3a			
C	-6.33107522894301	3.50007698796155	15.64773067436062
C	-7.36571855499739	2.62467469381182	16.37478233761425
H	-7.63463762501520	1.72912542322256	15.77719114922601
H	-8.29337881973665	3.19084585341409	16.59538907353781
H	-6.93674266613469	2.26986970708451	17.33541505371184
C	-5.06129823203928	2.70088053833774	15.32433505630834
H	-4.31371474794868	3.32073563475989	14.78923093915114
H	-5.28478153858495	1.80692394305868	14.70861338399203
H	-4.59764803042370	2.35582752089365	16.27224512451166
C	-5.99509847169400	4.76246494594249	16.45645128778044
H	-5.47432956570830	4.47287739264662	17.39283997286771
H	-6.91044973063888	5.32333526633313	16.72943990548784
H	-5.32321846061475	5.44350137813750	15.89242062116032
C	-9.07470501418903	2.09026903431690	13.17169691640829
C	-9.72916544213987	1.44816891320725	14.40996747077865
H	-10.77316164242974	1.16046008453078	13.16477189567864
H	-9.77114295362328	2.16706046770451	14.25488600931413
H	-9.19124025271880	0.53685066241825	13.74330576708405
C	-8.98994175170751	1.10154365553713	10.99326202844644
H	-10.01534864514319	0.79618464377731	10.69620995634801
H	-8.42178649016121	0.18483915109023	11.25388026637861
H	-8.51606867230839	1.57499361540641	10.10782664879887
C	-9.83963952551240	3.34448474077072	11.75779931456639
H	-9.39176717091856	3.82131855537684	10.86204685176569
H	-9.87133778295500	4.09574900170970	12.57489709961129
H	-10.88733953676249	3.07477911272779	11.50862876378948
C	-4.80457363941632	2.80131662323667	10.48532334211759
C	-5.35779263245864	1.77168082040276	9.48587828263437
H	-5.96251852375095	2.25680749118584	8.69222266578572
H	-5.98678007981312	1.01050459908902	9.99182750881007
H	-4.51376849406189	1.23961400954813	8.99923389785679
C	-3.99468520603507	2.12005644836830	11.59680252302976
H	-3.11539202106352	1.61241414209189	11.14830458013496
H	-4.59373775854449	1.35686296735394	12.13260428612055
H	-3.61833744355258	2.85599290329749	12.33620350548849
C	-3.96663097502051	3.88297085465365	9.77976937573586
H	-3.07128525237693	3.41339674306380	9.32171451836288
H	-3.61266813521327	4.65417070205572	10.49601842299945
H	-4.54092210917630	4.39053575155746	8.97797299947778
C	-4.04420868356082	9.32399009521783	12.46063036855732
C	-2.89887424666734	8.39094622461198	12.02568037041519
H	-3.27595882059397	7.55975429795606	11.39191301937957
H	-2.37243958628871	7.95009818666306	12.89724055925486
H	-2.15550528856673	8.95657458600056	11.42415403743204
C	-3.52952246143066	10.44734164536310	13.37801317731601
H	-3.01547006036212	10.04495147866231	14.27536243559276
H	-4.36022703626137	11.10192945015663	13.71623954759963
H	-2.80568523753971	11.08474974404730	12.82630220683131
C	-4.75600680424811	9.91186256337720	11.23600816439032
H	-4.04105033928644	10.51776211960138	10.63836504284659
H	-5.59699113473641	10.56988398621728	11.53481004807202
H	-5.15661514366623	9.11509595948685	10.57548003616175
C	-7.44461021294042	9.45382551622819	15.56303322011517
C	-7.12168879513008	8.13994045531735	16.27901231470832
H	-6.05147472533217	7.87079528517575	16.18103737539233
H	-7.72683116405463	7.30344428749467	15.87059146972799
H	-7.36026662814106	8.22825240818024	17.36082054209215
C	-6.56623262143266	10.59419748508114	16.11109526787938
H	-6.74756688166567	10.71897564201134	17.20019006994272
H	-6.78730652275099	11.56116559353660	15.61370681523833
H	-5.48615562625826	10.37286689076838	15.97687898438126
C	-8.94054560474948	9.78138064236856	15.71263540852162
H	-9.57551128098108	8.94008597711810	15.36462388880481
H	-9.22464473981591	10.69839351497342	15.15610157212300
H	-9.17622111581049	9.94921778391458	16.78566706663674
C	-9.30374838058693	8.10902628701062	11.65316214330597
C	-8.58465328503652	8.81601522253615	10.49858794199132
H	-9.33185149380273	9.16559664877687	9.75431669521743
H	-7.89095958180366	8.13035930850371	9.97242535924378
H	-8.01508965154344	9.69740799768378	10.85726130527214
C	-10.28720429957053	9.05503365139655	12.36604796779940
H	-11.07351468955078	9.36686798975623	11.64602070880924
H	-9.78230886265603	9.97333889507289	12.73049091468392
H	-10.78249547853674	8.55160452416231	13.22202269953582
C	-10.03667059801652	6.84880269260673	11.17381530174848
H	-10.62975328665525	6.39410664352439	11.99183561602277
H	-9.32189512360180	6.09271416822590	10.79034380623418
H	-10.71969200317348	7.10292024601082	10.33681345220537
P	-7.17716713020678	4.10675636983430	14.06442624518969
P	-7.25357729143957	2.33380043236224	12.69724309518508
P	-6.29242863002422	3.70458401485610	11.21670507587707
P	-5.50469741258406	5.02528652210656	12.84014122781481
P	-6.17927212681451	6.96753994442272	11.98895638093101
P	-5.17185910021580	8.23824021161218	13.56115256044706
P	-7.08181567336957	9.43283896963901	13.67967428868363
P	-8.09743649445940	7.54599707611740	13.01330907878982
Cl	-11.06353378323448	6.33565009501673	15.16290018924647
Cl	-8.43843276617138	5.95876188920335	7.83221520769500
Au	-8.95509586389566	5.50779276602104	14.38190158517696
Au	-7.43131940724605	4.84246463392884	9.61956566624752

Rotamer 3b			
C	6.338992	-0.254311	0.742028
C	6.107668	-1.329154	-0.331867
C	6.597274	-0.837136	-1.699573
P	4.239874	-1.719160	-0.296722
Au	3.423266	-1.683265	2.238508
Cl	4.628663	-3.578764	3.046117
P	3.341177	0.054306	-1.359313
P	2.257480	-1.536830	-2.515810
C	2.352909	-0.994691	-4.326007
C	1.856244	-2.188024	-5.159418
P	1.844872	1.053843	0.040571
P	2.123446	0.184831	2.092965
C	2.686692	1.629739	3.176636
C	1.768671	2.844223	2.977232
P	-0.088600	0.006186	2.327342
C	-0.423336	-1.788293	2.916898
C	0.140658	-2.886152	2.014674
P	-0.041088	-0.180166	0.074966
C	-1.369455	1.067795	-0.492126
C	-1.191344	1.219313	-2.011268
P	3.941627	-2.958307	-2.163033
C	3.149004	-4.577011	-1.507908
C	2.283704	-4.417245	-0.257478
C	1.415479	0.214366	-4.462067
C	3.793865	-0.621860	-4.702840
C	6.791226	-2.653842	0.053250
C	2.326843	-5.136769	-2.681648
C	4.355869	-5.484526	-1.195549
C	-2.710961	0.390852	-0.156447
C	-1.255928	2.431061	0.201053
C	0.176210	-1.874245	4.331021
C	-1.961553	-1.886744	2.959356
C	2.628748	1.125940	4.628514
C	4.127257	1.949868	2.750457
H	7.418688	0.000827	0.791838
H	5.784411	0.678110	0.507610
H	6.022419	-0.606486	1.745180
H	7.885359	-2.490431	0.154919
H	6.404543	-3.051455	1.014783
H	6.643445	-3.424155	-0.732168
H	7.692851	-0.655291	-1.657776
H	6.405142	-1.586637	-2.493674
H	6.104417	0.112745	-1.990271
H	2.973194	1.930897	5.311139
H	1.593962	0.854695	4.922139
H	3.278847	0.239844	4.777159
H	4.507770	2.807879	3.343001
H	4.800828	1.086836	2.920195
H	4.179936	2.233680	1.677932
H	2.109730	3.671673	3.634324
H	1.794622	3.207082	1.929902
H	0.718058	2.607759	3.240353
H	-0.088501	-2.851697	4.787076
H	1.284618	-1.809700	4.300922
H	-0.208323	-1.073113	4.995965
H	-0.041537	-3.879114	2.478109
H	-0.337541	-2.884927	1.015625
H	1.238081	-2.782640	1.879089
H	-2.253746	-2.866723	3.393149
H	-2.415979	-1.088163	3.581372
H	-2.395723	-1.834707	1.939790
H	-2.069411	3.097857	-0.157837
H	-1.352116	2.336619	1.301492
H	-0.287675	2.922981	-0.023179
H	-3.546483	1.009732	-0.547670
H	-2.783914	-0.621771	-0.605197
H	-2.851132	0.301879	0.941004
H	-1.958399	1.915448	-2.411644
H	-0.194660	1.638094	-2.262717
H	-1.304143	0.246949	-2.533370
H	3.990332	-6.490910	-0.899725
H	5.025637	-5.607565	-2.071531
H	4.949518	-5.086848	-0.346918
H	1.939719	-6.143013	-2.415271
H	1.451219	-4.490243	-2.902898
H	2.934893	-5.238979	-3.604471
H	1.803055	-5.387766	-0.010445
H	2.882722	-4.102360	0.619353
H	1.470869	-3.676578	-0.411746
H	1.441144	0.588342	-5.506837
H	0.369390	-0.054981	-4.216419
H	1.729867	1.048484	-3.799705
H	3.825293	-0.320163	-5.770876
H	4.167002	0.228202	-4.096740
H	4.483752	-1.478980	-4.567631
H	1.860632	-1.912333	-6.234845
H	2.515883	-3.071238	-5.035452
H	0.824020	-2.479766	-4.877530
Au	0.164337	-2.077295	-1.788817
Cl	-1.988709	-3.075725	-1.543658

Complex 4			
C	-6.42796653075706	3.47592382874835	15.70169983316478
C	-7.37873764173179	2.37599168037471	16.20558132641314
H	-7.41581201268211	1.51204371028168	15.51031012897350
H	-8.40822465266193	2.76114042010262	16.35272751039749
H	-7.00779714308590	2.00257046354359	17.18284155551935
C	-5.02118898631563	2.91905783770998	15.44646552182490
H	-4.32025197369473	3.71034314925223	15.11431191134459
H	-5.03544079409916	2.10350143661907	14.69557262743029
H	-4.61945538894342	2.50197972279533	16.39328150111806
C	-6.39913468094252	4.66136700555432	16.67554415694564
H	-5.91747567745796	4.34824296980370	17.62437896792050
H	-7.42150015364190	5.02583521882820	16.90058285444123
H	-5.80382522885210	5.50213563167957	16.26892888167881
C	-9.03214805032031	2.06523449377938	13.14917255564572
C	-9.71749046507995	1.38031249422799	13.34682481047994
H	-10.74501999744556	1.07824262147110	13.05453779300597
H	-9.80676299769276	2.07560388448869	14.20706381749457
H	-9.17380535608414	0.47187121625514	13.67770753468916
C	-8.88914856267294	1.10656633388321	10.95145177708051
H	-9.89833495447412	0.78617108704305	10.61751905733177
H	-8.30912387644520	0.19643969045137	11.20861032973318
H	-8.40096733192309	1.60997501078479	10.09063391484361
C	-9.80712461272098	3.31510152372628	11.73955875234132
H	-9.34238293441362	3.82002871155601	10.86784188707741
H	-9.87862774214942	4.04784625974187	12.57083616404545
H	-10.84101291992297	3.03151543068848	11.45204594502835
C	-4.73296889979166	2.82427725357600	10.56768370920512
C	-5.23100686761109	1.78431711490779	9.55030595637814
H	-5.82273861551248	2.25681614449718	8.73959188993321
H	-5.85592891972868	1.00687044036890	10.03560303646009
H	-4.35985180235799	1.27450446048305	9.08868438956005
C	-3.94218879073213	2.16350981939558	11.70529798274996
H	-3.02902157612003	1.69098234126045	11.28768720618206
H	-4.53381684822947	1.37501432467454	12.21164917819129
H	-3.61900489461422	2.90557002038219	12.46388773009220
C	-3.90271730748201	3.92983708027900	9.89015815009047
H	-2.98719378291693	3.48344041063475	9.44977404519022
H	-3.58027328939887	4.70103815791945	10.62120545173151
H	-4.46870967068590	4.43203117373586	9.07914126555069
C	-4.07089649098387	9.34312983491773	12.26721066077433
C	-2.99810705298255	8.37893588142771	11.73113603724090
H	-3.44663076994173	7.58479065331739	11.09770133142821
H	-2.43399685903932	7.89331153439589	12.55356616779980
H	-2.27820006349729	8.94220353621936	11.10182129007525
C	-3.46693926795442	10.40486374794513	13.20164825511485
H	-2.90954619937504	9.93860208594232	14.03976272267865
H	-4.25084750663533	11.06611024194861	13.62537573142584
H	-2.76115312771172	11.04222706745468	12.62930874155244
C	-4.85732265313108	9.98815792884952	11.11705677884677
H	-4.16265404577203	10.58075666880615	10.48614134780146
H	-5.64469963636452	10.67079354584345	11.49437853343195
H	-5.33345379241031	9.22517899476716	10.46712483063090
C	-7.34134568040028	9.47536007295065	15.58164861497369
C	-7.24173861088586	8.11990991771132	16.28040369156481
H	-6.23677165848065	7.66668142788239	16.15438945770349
H	-7.99614758110625	7.40184056278027	15.90010426295578
H	-7.41487075852832	8.24822753913551	17.36963351522634
C	-6.25706082849764	10.43523984755884	16.10407724760219
H	-6.40082757198035	10.59861034918815	17.19297384202363
H	-6.29747135469924	11.42383364890082	15.60210043197187
H	-5.24105923661838	10.00840698159774	15.96497950455924
C	-8.75548747194127	10.05777446449014	15.77342266028000
H	-9.53121691145134	9.34996752611751	15.41536955814693
H	-8.88572171506859	11.02689756193912	15.24951842572611
H	-8.93654984999923	10.22701354720682	16.85596156079786
C	-9.34975112015655	8.12776597483273	11.70990668344654
C	-8.65885298042896	8.85825984753881	10.55266576664671
H	-9.42603526747723	9.22554533957490	9.83824700500980
H	-7.98378094731325	8.18267605180467	9.99017155059747
H	-8.07956888483318	9.73284817685355	10.91195364164288
C	-10.32093483462700	9.05557119174003	12.46310820978609
H	-11.12824264378037	9.37221229304416	11.76929166770660
H	-9.81533733455747	9.97482514164688	12.82534485801803
H	-10.79046350222923	8.53528546592131	13.32383010237943
C	-10.08343114365139	6.86975433145179	11.22134246926602
H	-10.66422532977642	6.39937886352319	12.03895831891745
H	-9.37393168180972	6.12343371497887	10.81096977322653
H	-10.78073629084123	7.13895534988352	10.40117670181229
P	-7.19804714650779	4.11161143790947	14.09028128309854
P	-7.22956688810287	2.32864663608698	12.73277947273357
P	-6.25925033645456	3.69075021045973	11.25686385387252
P	-5.51311060121637	5.04598094139456	12.88362943826794
P	-6.27281546984798	6.90908416779969	11.90583047959453
P	-5.22668826881773	8.29449852732405	13.32200673572989
P	-7.09746558351496	9.45084476420363	13.68192626830528
P	-8.12293651930710	7.54345062350502	13.04162252349809
Cl	-11.10818436501078	6.32685275662736	15.12144312591890
Cl	-8.40285890497424	5.99209316368751	7.90044573010258
Cl	-2.84041817658450	5.95850049231975	16.49188408830228
Au	-9.00484192176386	5.47070500486621	14.38978450622693
Au	-7.39352935657367	4.83797421495646	9.65994727295933
Au	-4.12401287689289	7.13567957126538	14.93651516331619

Table S11. Cartesian coordinates of the optimized transition state structures for the Y-shape coordination flip for complexes **2** and **4**.

Complex 2 (Rotamer 2a)

C	6.358460	2.274347	9.994087
C	5.727252	3.389226	10.850759
C	6.413599	4.726358	10.566111
P	5.912992	2.767100	12.655164
P	7.917908	3.570604	13.325634
C	8.836898	2.000360	13.922739
C	7.974714	1.053539	14.766003
P	5.067556	4.425203	13.900543
C	3.640095	3.692066	14.916206
C	4.028158	2.347086	15.544448
Au	4.833044	6.664762	13.094372
P	6.703976	7.686654	14.178858
P	7.817706	6.207220	15.456146
P	6.877028	4.217383	15.220565
C	4.214677	3.493551	10.592080
P	6.504843	8.960823	16.008998
C	4.666270	9.505621	16.011436
C	3.659947	8.354005	15.979339
C	8.033199	8.484004	13.082505
C	8.395853	7.424997	12.029905
P	6.512363	6.992438	17.121599
C	7.804764	7.276133	18.505567
C	8.128425	5.864874	19.031368
C	7.086946	8.114797	19.577920
C	9.080941	7.983763	18.035647
C	7.366546	9.706311	12.429388
C	9.264663	8.895206	13.899970
C	9.321596	1.293465	12.644547
C	10.024185	2.532633	14.746874
C	2.463747	3.527685	13.939384
C	3.319627	4.735345	15.997662
C	4.490302	10.410120	14.779962
C	4.509935	10.311786	17.315770
H	7.524603	7.183178	11.391046
H	8.749689	6.480956	12.496808
H	9.207134	7.809656	11.376446
H	8.071749	10.173592	11.709725
H	7.097694	10.473229	13.183978
H	6.447484	9.419637	11.878081
H	9.751362	8.015600	14.368090
H	8.998473	9.612445	14.702616
H	10.006948	9.382962	13.232235
H	8.611271	5.243430	18.247305
H	7.216686	5.334898	19.376582
H	8.833083	5.930533	19.888041
H	7.744393	8.240327	20.464965
H	6.145115	7.635092	19.916400
H	6.844106	9.129343	19.197903
H	9.781391	8.105314	18.890270
H	8.858372	8.990559	17.627564
H	9.602083	7.400672	17.248833
H	2.624174	8.756320	15.972425
H	3.770833	7.688285	16.857531
H	3.784211	7.736472	15.063313
H	4.579732	9.828373	13.839255
H	5.233338	11.234516	14.761761
H	3.477354	10.866213	14.794036
H	3.480329	10.724392	17.380409
H	5.223638	11.159853	17.365812
H	4.668138	9.671180	18.208612
H	3.161808	1.938321	16.107521
H	4.874239	2.459808	16.252446
H	4.318308	1.606508	14.771934
H	2.691797	2.779905	13.152770
H	2.208356	4.488165	13.446475
H	1.568565	3.172588	14.492781
H	2.519341	4.349789	16.664031
H	2.965436	5.682276	15.546583
H	4.206989	4.966871	16.624890
H	8.576613	0.173374	15.080259
H	7.100010	0.685067	14.192575
H	7.599735	1.553906	15.682352
H	9.928905	1.966619	12.004392
H	8.465629	0.920146	12.043860
H	9.949700	0.416132	12.910262
H	9.675597	3.078563	15.649442
H	10.661594	3.220805	14.154018
H	10.657916	1.687212	15.090934
H	6.244543	5.021776	9.508366
H	7.505278	4.672993	10.745279
H	5.999729	5.533362	11.208689
H	6.242629	2.518784	8.916407
H	5.878848	1.290628	10.176795
H	7.445331	2.174165	10.197172
H	3.760201	4.305797	11.196410
H	3.688542	2.542871	10.818876
H	4.035594	3.734690	9.522504
Cl	3.190412	7.621972	11.608221

Complex 2 (Rotamer 2b)

C	9.949406	7.361241	12.694746
C	10.082324	5.994420	12.002677
C	11.273983	5.204547	12.574062
P	10.571517	6.382712	10.187771
P	8.599884	7.101716	9.341949
P	8.869530	9.263646	8.700098
P	10.318105	9.279078	6.981063
P	11.632169	10.676625	8.134849
C	13.338429	9.815839	8.112320
C	14.207498	10.645247	9.075715
C	8.783978	5.193732	12.153983
P	10.066901	4.434846	9.127770
C	11.721338	3.818013	8.369690
C	11.356145	3.115459	7.051377
P	10.639623	9.841418	9.984324
C	10.004541	11.437089	10.837700
C	11.259170	12.077829	11.459234
P	9.243964	5.848961	7.601620
C	7.635034	5.146596	6.879143
C	8.042182	4.196299	5.740240
Au	10.692480	7.100234	6.118139
C	9.030151	10.962472	11.930386
C	9.307187	12.427135	9.897807
C	12.757201	4.913742	8.120914
C	12.254070	2.801655	9.399115
C	9.503466	10.364877	5.645958
C	10.607858	10.633943	4.609098
C	8.363723	9.534781	5.038283
C	8.964947	11.679720	6.223606
C	13.302125	8.350316	8.547010
C	13.841907	9.930521	6.662803
C	6.879186	6.364899	6.325132
C	6.807203	4.418956	7.945016
H	9.098098	7.937148	12.276011
H	10.864791	7.976205	12.578105
H	9.757248	7.220808	13.780381
H	8.573896	5.017484	13.231494
H	8.853288	4.208714	11.649858
H	7.919799	5.739187	11.722280
H	11.522112	1.991797	9.597936
H	12.498893	3.292090	10.364287
H	13.187311	2.335732	9.016393
H	11.120325	5.015387	13.658305
H	12.229975	5.755615	12.454916
H	11.378072	4.217480	12.076761
H	7.590679	9.296045	5.797260
H	8.741937	8.583417	4.609452
H	7.873544	10.109159	4.224207
H	8.510206	12.282641	5.408755
H	9.773766	12.281235	6.684122
H	8.184953	11.496428	6.989709
H	13.854458	10.981653	6.306850
H	13.209107	9.331378	5.974541
H	14.877402	9.533861	6.593439
H	10.196244	11.246957	3.779389
H	11.003878	9.689964	4.182237
H	11.452516	11.198409	5.055957
H	6.636580	7.095204	7.126705
H	7.471864	6.884094	5.546985
H	5.921902	6.037119	5.867784
H	5.871738	4.029745	7.488520
H	7.364490	3.563558	8.376953
H	6.528936	5.101057	8.774157
H	13.680201	4.469720	7.689574
H	12.379994	5.663388	7.394847
H	13.028104	5.445979	9.053792
H	10.560663	2.354024	7.192988
H	11.024596	3.846322	6.285463
H	12.251449	2.596677	6.646370
H	7.133137	3.841000	5.210334
H	8.698835	4.703098	5.003304
H	8.577280	3.306447	6.126547
H	8.163101	10.423221	11.492279
H	9.524583	10.291265	12.660409
H	8.631157	11.837517	12.486863
H	8.988120	13.326643	10.468026
H	9.983569	12.759753	9.085121
H	8.403732	11.978578	9.437484
H	14.323134	7.913670	8.501654
H	12.910921	8.229027	9.576315
H	12.652157	7.752428	7.878095
H	14.252754	11.713496	8.778721
H	13.821449	10.588145	10.115370
H	15.244587	10.246524	9.083678
H	10.972106	12.968978	12.057769
H	11.793138	11.373491	12.130496
H	11.968662	12.417256	10.675526
Cl	11.843296	6.152852	4.222328

Complex 4

C	0.602710	-3.404761	-4.343435
C	-0.418327	-2.420298	-3.743070
C	0.045797	-0.979691	-3.943947
P	-0.609459	-2.994027	-1.928196
P	1.285793	-2.432515	-0.901163
C	2.042458	-3.982909	-0.141436
C	0.957493	-4.799023	0.574091
P	-1.499567	-1.249800	-0.811830
C	-3.065529	-1.974228	-0.017085
C	-2.752004	-3.175547	0.882469
Au	-1.712817	1.010776	-1.562530
P	0.128969	2.002575	-0.426216
P	1.385292	0.459920	0.678778
P	0.151720	-1.413096	0.729219
C	-1.819867	-2.618136	-4.351195
P	0.040929	3.287035	1.420642
C	-1.808032	3.668227	1.729990
C	-2.783014	2.520881	1.476845
C	1.309987	2.952845	-1.572271
C	1.385786	2.159432	-2.883146
P	0.487624	1.397943	2.510660
C	1.921358	1.740043	3.689088
C	2.416979	0.370332	4.191723
C	1.354102	2.590965	4.840465
C	3.033696	2.484467	2.933200
C	0.622084	4.310601	-1.803102
C	2.694304	3.130300	-0.936968
C	2.668653	-4.778936	-1.299118
C	3.110670	-3.480526	0.847387
C	-3.940326	-2.388893	-1.214875
C	-3.732247	-0.836328	0.767431
C	-2.111435	4.841648	0.777791
C	-1.862173	4.110294	3.204448
H	0.393759	2.089313	-3.372717
H	1.771201	1.134967	-2.711896
H	2.088574	2.660410	-3.580133
H	1.218441	4.893759	-2.535574
H	0.564141	4.908700	-0.870176
H	-0.400067	4.187762	-2.216411
H	3.207959	2.158489	-0.796171
H	2.631426	3.655584	0.037194
H	3.329991	3.741059	-1.611939
H	2.647552	-0.327860	3.341051
H	1.668346	-0.124504	4.872008
H	3.358897	0.528549	4.778663
H	2.155961	2.784064	5.583786
H	0.523479	2.070801	5.362274
H	0.986992	3.575529	4.479942
H	3.873039	2.682838	3.633932
H	2.682861	3.461067	2.535398
H	3.433551	1.878546	2.090580
H	-3.821208	2.864558	1.666624
H	-2.589059	1.658279	2.147609
H	-2.733730	2.161292	0.428081
H	-2.064000	4.520758	-0.283110
H	-1.413084	5.691004	0.923912
H	-3.142027	5.208151	0.967969
H	-2.882663	4.480211	3.438077
H	-1.144954	4.928134	3.423012
H	-1.654111	3.261928	3.890427
H	-3.703221	-3.617188	1.248164
H	-2.171357	-2.875976	1.777542
H	-2.199071	-3.965123	0.334484
H	-3.485236	-3.221327	-1.790431
H	-4.126768	-1.536768	-1.900563
H	-4.921385	-2.744007	-0.835863
H	-4.659063	-1.212571	1.247569
H	-4.000293	0.010644	0.104212
H	-3.075609	-0.460805	1.576873
H	1.423790	-5.692346	1.039862
H	0.177639	-5.150541	-0.130854
H	0.473847	-4.216049	1.383499
H	3.432134	-4.183153	-1.840821
H	1.900801	-5.114997	-2.025985
H	3.164644	-5.684747	-0.892048
H	2.666808	-2.839747	1.637237
H	3.907032	-2.906313	0.329878
H	3.583711	-4.353900	1.343120
H	0.091978	-0.750847	-5.029179
H	1.058175	-0.812790	-3.522714
H	-0.649191	-0.252123	-3.476033
H	0.679209	-3.231300	-5.437460
H	0.308692	-4.462864	-4.185363
H	1.614326	-3.248005	-3.913237
H	-2.552830	-1.911855	-3.910172
H	-2.195267	-3.652540	-4.211459
H	-1.776140	-2.413284	-5.441512
Cl	-3.337242	1.952433	-3.046971
Au	-1.129328	0.067824	3.393759
Cl	-2.594563	-1.469279	4.373743
Au	2.867942	-1.061847	-1.781323
Cl	4.643117	0.226296	-2.576288

Table S12. Cartesian coordinates of the optimized structures for the monodentate monometallic complexes according to table Table S8.

Coordination on α-P

C	2.00042778068444	1.12661072523987	5.04619997975187
C	2.32505330998598	1.88146986840759	3.74597554104540
C	3.79198352774302	2.35957247255969	3.73068937899146
C	1.37931333483904	3.07027028102772	3.55042471270745
P	2.28594350122092	0.58169467493019	2.34509351740178
P	1.99147704134931	1.82925063263381	0.47242753549241
P	3.35639704460710	0.54028372314759	-0.73770319093409
P	3.07397241373721	1.86009380515578	-2.55100083429032
C	3.02966358586908	0.60726395661912	-3.99170797604176
C	1.61686765982238	-0.00303020020187	-3.93816176043562
P	0.14623713990850	-0.00587693253689	2.07119611288286
C	0.11841285936365	-1.89554026401681	2.07404896289556
C	-1.28785737025925	-2.30809897806745	1.60804437701711
P	0.16103177786647	0.60658129088621	-0.07891203115664
C	-1.20789676453780	1.92331151440493	-0.29020665426967
C	-0.98964133292927	2.41657095984056	-1.73590674375868
C	-2.54824810701405	1.18167850364298	-0.15239371358333
C	-1.13049472887874	3.09941608865327	0.68796018991557
C	1.19672566737967	-2.43931692845007	1.12424365438112
C	0.38957743520309	-2.33092345309586	3.52368625202236
P	5.25818762592072	2.39171996315904	-2.36024897233079
C	5.18730214242584	4.30312212992662	-2.26012188675122
C	4.92666445602943	4.77997812794617	-3.69997456773206
P	5.13680441328101	1.81602604662899	-0.18228203336484
C	6.53246929147485	0.52947723379176	0.02888194755541
C	6.26800977627013	-0.11585404903419	1.40169464010009
C	7.84227048178256	1.33734668929711	0.03646248986976
C	6.56513030880148	-0.53748882275980	-1.07124567976407
C	3.22801588405073	1.44138458118233	-5.26981862534326
C	4.09502895733551	-0.49051677364615	-3.89601430098673
C	4.10031371038206	4.83402155059647	-1.31543725391693
C	6.58079848408004	4.73932366408838	-1.77383238348148
H	2.12884201739228	1.80575199714166	5.91569733653075
H	0.94736215251972	0.77176912499246	5.05416129462266
H	2.66719045617650	0.25207439115900	5.19403526486293
H	1.50786790702637	3.79035799469303	4.38662215493424
H	1.58642331691635	3.60573046911958	2.60202672893255
H	0.31657658394750	2.74880325763373	3.54744817181855
H	3.94159885075450	3.12911378852179	4.51760926301805
H	4.49627712569101	1.52531741894294	3.92598153397440
H	4.06206069253151	2.81340221176738	2.75307146305612
H	0.38437379413145	-3.43934855477600	3.58633996471985
H	1.38355530936965	-1.97935151994423	3.87170807981593
H	-0.38206118821023	-1.93958538372235	4.21810262895346
H	1.16793564053662	-3.54917254129061	1.13381461366716
H	1.03151804806349	-2.10006150712994	0.08159130649747
H	2.21185662213922	-2.11895949899473	1.43432890194682
H	-1.36220342405191	-3.41556887894513	1.58553277101619
H	-2.07335060712122	-1.92080008198258	2.28906950019916
H	-1.49908568815443	-1.93599605623337	0.58350319217937
H	-3.38450505153687	1.87119750690216	-0.39538822872644
H	-2.61298317218521	0.31137463346017	-0.83778021213572
H	-2.70418525225213	0.82318990360145	0.88773256021375
H	-1.92859334622708	3.83501618705964	0.45075951454965
H	-1.28530727187284	2.76699213805439	1.73591678738720
H	-0.15397416980765	3.62063269597946	0.62614903052700
H	-1.74012582406442	3.19823779571077	-1.97993899811478
H	0.02052419379570	2.86032793318270	-1.86684819591213
H	-1.09858321306990	1.59285371274176	-2.47047188308907
H	8.70436489477507	0.66299146183554	0.22893124482349
H	8.01506643674759	1.83059932650601	-0.94341165272373
H	7.83879082721246	2.11970752103810	0.82364067819266
H	7.39704472717479	-1.25097740030954	-0.88400876691953
H	5.62035282008822	-1.11802249981281	-1.09954605204679
H	6.72209543206542	-0.08196860452372	-2.06973309117017
H	7.05095765685369	-0.87198274602987	1.62570306159560
H	6.27491185290385	0.63801010819479	2.21547042278950
H	5.28333211074046	-0.62988158363592	1.42334539593073
H	6.64353691118108	5.84841619366556	-1.74162808325416
H	6.78250116217951	4.36439615264954	-0.74796030359955
H	7.38561573220555	4.36998705332721	-2.44278249014821
H	4.12059232920569	5.94567813069622	-1.30162139547243
H	3.09015872639265	4.51181957270077	-1.63979035471018
H	4.25414069162210	4.47371750089842	-0.27793115108776
H	4.92213703744629	5.89066047348086	-3.73903879490954
H	5.70484871718235	4.41571715054406	-4.40235118936083
H	3.93777022213432	4.43019365807773	-4.06529732664084
H	3.14213256283630	0.79051188392805	-6.16648637849338
H	2.46861464539262	2.24587373444444	-5.35835207344073
H	4.23484242326499	1.90955283305558	-5.29116038322944
H	4.01390630738501	-1.17476609029588	-4.76863526594232
H	5.11705059773034	-0.06096381279690	-3.89075184061474
H	3.96832056868497	-1.09820218469810	-2.97667175320145
H	1.48767591990587	-0.73992675791332	-4.75987542933097
H	1.44125205497790	-0.53161090010571	-2.97684470013554
H	0.83255218407647	0.77375833467027	-4.04608393622269
Au	-1.42954355211388	0.84006390050312	3.46713378281178
Cl	-3.08441081048476	1.60486337031925	4.93026959724738

Coordination on β-P

P	0.12124176635390	0.29063998556102	-0.29781244801520
P	0.11658960115917	0.04828377290277	1.95900161316365
P	2.29667688062546	0.49970352293338	1.85931938997602
P	2.06156788338641	1.45024421695717	-0.15724104150251
P	3.19986470127344	-0.20059486227292	-1.15484924518926
P	2.31231003384638	0.32006920925403	-3.16470491032876
P	4.42252917256635	0.80077241208637	-3.81712937511381
P	4.96242105180946	1.12860815372461	-1.65328475910913
C	6.48667209467900	0.00633128735490	-1.38779034035787
C	2.01372093651444	-1.40116387553146	-3.94755538886034
C	4.21704728464898	2.60363030607584	-4.43659996781911
C	-1.17502545406685	1.66971262377521	-0.56129536150561
C	-0.00595415842489	-1.85130913413754	2.18206106825839
C	2.71059580450706	1.82566534117913	3.12877240836275
Au	3.80129262484170	-1.20981541374753	1.82398378108913
Cl	5.34870357578912	-2.96619134243560	1.87590941348556
C	1.83193127258413	-1.13152985977687	-5.45222566565572
C	3.16179626448276	-2.38984558554576	-3.71276477843325
C	0.71386923851116	-1.93457874118815	-3.32153214458903
H	2.76159557103080	-0.72448123723498	-5.90316390411248
H	1.58950952820779	-2.07869725251328	-5.98051029480394
H	1.00805128610340	-0.41315246304959	-5.64425586316406
H	2.92475309346772	-3.36631731508075	-4.18869949772798
H	4.11085358685158	-2.01792135315109	-4.14886535542242
H	3.32473403821398	-2.57122490537266	-2.63038384520665
H	0.45698778254710	-2.91908293636462	-3.76861585108777
H	0.82030591812780	-2.07037293131082	-2.22575205290085
H	-0.13750040383880	-1.24393075610618	-3.49036426305980
C	2.65348084360063	1.14857830169449	4.50811670210259
C	4.13525252200118	2.29564150498771	2.78353219570008
C	1.70615989263008	2.98191015936303	3.02999835452462
H	2.92316270926627	1.88320513847392	5.29564346335948
H	1.63378390264720	0.77157452956996	4.73130638602853
H	3.36268979842538	0.29757248680735	4.57155006652184
H	4.43731166211899	3.10747744598652	3.47785920126514
H	4.86842851581490	1.46860750001625	2.87551311111392
H	4.19284186483242	2.69433189665197	1.74845942244478
H	1.96469645287068	3.76119228551137	3.77735756690498
H	1.72667393335542	3.45341092458131	2.02640190032233
H	0.67201085306435	2.63934935382598	3.23523935651723
C	0.59105975916474	-2.16313407159663	3.56493704022568
C	-1.52416924187709	-2.12251890955961	2.16390567820822
C	0.68331048513174	-2.67399857010850	1.08717373717545
H	0.42457113713398	-3.23336618489856	3.81115959705699
H	1.68780626569407	-1.98600653175751	3.58031893350842
H	0.12456010947071	-1.55191027750801	4.36522785979463
H	0.56619262958475	-3.75689605155936	1.30607900071589
H	0.24557679338462	-2.47118684118904	0.09002412623515
H	1.77213116266507	-2.45812617181486	1.02912485634288
H	-1.71050885033752	-3.20617023773509	2.32197861754066
H	-2.05508843749170	-1.56218297184612	2.96057860550432
H	-1.97243870324067	-1.84845910004945	1.18561269035283
C	-2.53493908781532	1.00106197029751	-0.29005780311179
C	-0.98359909203763	2.88976393429946	0.34672523629831
C	-1.04054708705440	2.07187763279638	-2.02413787317093
H	-1.77338586877537	3.64384860970322	0.13864862410392
H	-1.05046837455277	2.61325473638356	1.41817265591688
H	-0.00121038630575	3.37437288942618	0.17114406276410
H	-3.35804006955115	1.71637804756067	-0.50309837891188
H	-2.68780713086184	0.10550624652671	-0.92735367516776
H	-2.62871761301860	0.69372884062157	0.77309534592083
H	-1.80327992534591	2.83966470166299	-2.29337803633507
H	-0.03910922694555	2.49980162809351	-2.25524155181491
H	-1.18383104312898	1.20504183707637	-2.71804633061690
C	5.64440258471041	3.16140639212711	-4.57368982532279
C	3.53117933193199	2.49141300840383	-5.80957783561116
C	3.38539473611789	3.48673837495242	-3.49574854995531
H	3.41801260681044	3.49981319895012	-6.26305185163353
H	4.11668406830675	1.86347818883208	-6.51274450990750
H	2.51516828608193	2.05253073234255	-5.71541240887628
H	5.61220699558065	4.19453613534734	-4.98211964506127
H	6.15325995426719	3.20829291706240	-3.58761022072608
H	6.26513041212526	2.54285127993828	-5.25456062479921
H	3.30971532418465	4.51608791816299	-3.90937430292910
H	2.35721754091251	3.08817443404849	-3.37481151322870
H	3.84667103549991	3.55274159042078	-2.48918232238774
C	6.85069610723574	0.18537945587591	0.09785461961547
C	6.23296111425539	-1.46950817096006	-1.71380162356043
C	7.59228324959602	0.57958824406854	-2.29190091957181
H	7.72632632238259	-0.44704659239711	0.35732485090047
H	7.09876754574842	1.24095682096062	0.33195919708056
H	6.01445968355760	-0.12991896625500	0.75809757852579
H	7.16103647538755	-2.05837717514173	-1.54688663159338
H	5.44810581047420	-1.90075414240716	-1.06018582567329
H	5.92942603850826	-1.60051849003996	-2.77183954022912
H	8.54256829062648	0.03050096484809	-2.11768111526217
H	7.33105998158944	0.47182166313022	-3.36577323408073
H	7.77950736749323	1.65410531281912	-2.08474480542399

Coordination on γ-P

C	2.34851937857476	1.19876404175248	4.86879554375585
C	2.46253690677708	1.93554476351502	3.52215226280186
C	3.87288039964281	2.51955095660023	3.33042665119966
C	1.40510490900620	3.04211657302263	3.42655653212195
P	2.28223529931965	0.57299466474533	2.18642423104152
P	1.80248677151042	1.79094337456360	0.34949894279248
P	3.25279450305866	0.74336241976637	-0.95035306730011
P	3.14673390209373	2.05886023404627	-2.75494691355731
C	3.16272544777499	0.88905736678271	-4.26467660802544
C	1.77380942261608	0.22465410663640	-4.27390274277407
P	0.06725349088078	0.11359090069877	2.24242296123338
C	0.02493291846130	-1.78453807752919	2.47536468319041
C	-1.43323360996073	-2.19412371260012	2.19859617644902
P	0.10063879366319	0.35268172717057	-0.00244840778366
C	-1.33281780583710	1.56353021996262	-0.36710169570055
C	-1.06860606538677	2.04482991289083	-1.80626415600235
C	-2.61821377538130	0.72060361703838	-0.28897049300102
C	-1.40909989051609	2.75228303575889	0.59830728363634
C	0.97744736436430	-2.54649853949312	1.55079505443009
C	0.39626993727818	-2.02630464065412	3.94936047717766
P	5.33358688458617	2.48583214340086	-2.35739577073555
C	5.27731377264965	4.37614266150744	-2.05274835026875
C	5.08219369454072	5.00646180708507	-3.44335971806853
P	5.12153935500662	1.72366607136859	-0.23321540762568
C	6.42578839084737	0.33249765639754	-0.10199391298542
C	6.01186965781705	-0.51213546788664	1.11590775792404
C	7.73787157544311	1.09530926809042	0.16928041194062
C	6.57028304399355	-0.54650165953461	-1.34760900953531
C	3.33102283743841	1.84246636461883	-5.46449219527989
C	4.27291042314505	-0.16572006890505	-4.26590424372213
C	4.16046814791951	4.82299294185502	-1.09880755381918
C	6.65601252232411	4.73390243929158	-1.46932124690771
H	2.52319992001329	1.91034575847066	5.70415244994491
H	1.33640288456464	0.76408598992189	5.00654176445993
H	3.09405605419456	0.38124896300507	4.95635169101817
H	1.55471560146713	3.77837100864603	4.24592756648773
H	1.47618214246892	3.58911058264016	2.46391739957099
H	0.37952987939934	2.63007958311008	3.51690625018860
H	4.06699738404902	3.30078122567967	4.09654395034462
H	4.65650636561132	1.74040796296460	3.42831274958463
H	3.98822688810916	2.98465094037571	2.32902226295345
H	0.31452535798694	-3.10897730923092	4.18581847534377
H	1.44329308206910	-1.71967045731588	4.15483468154329
H	-0.27122208429307	-1.47327485701568	4.64247352712160
H	0.92410432270224	-3.63797727036328	1.75303261239032
H	0.72121727814250	-2.38958552972269	0.48466975825242
H	2.02929199802684	-2.22476885790384	1.69334120414105
H	-1.56008117272520	-3.28369820828384	2.37621534427179
H	-2.14755161285639	-1.65435896110757	2.85445840003777
H	-1.71233987479071	-1.99606290327558	1.14221445380137
H	-3.49517396219182	1.33666805897146	-0.58251182771238
H	-2.57663142382330	-0.15802603506544	-0.96574163831543
H	-2.79693385437167	0.35606495090274	0.74431404461485
H	-2.27007986046653	3.40307433304811	0.33145485835087
H	-1.54481903405445	2.41239175565983	1.64509517488735
H	-0.48957115214126	3.37147032973453	0.55222461904213
H	-1.87135583192547	2.74140375838383	-2.13032778071015
H	-0.10140619749569	2.58816906069170	-1.88082163046033
H	-1.03931424911919	1.19708686862417	-2.52151099812564
H	8.56443041656901	0.37009315411470	0.32715061144263
H	8.01801669773046	1.73715618716622	-0.69259746437346
H	7.66541628434416	1.73468315888765	1.07318176682433
H	7.38668751449573	-1.28349165670384	-1.18993968204693
H	5.64078784371686	-1.11906190745726	-1.54873136188603
H	6.81547934164403	0.05400528504747	-2.24609828680079
H	6.79088598828031	-1.27635813155003	1.32308269995875
H	5.88415896632751	0.10799582501477	2.02648053263014
H	5.05521237693509	-1.04509173953049	0.92963801510569
H	6.72983762861539	5.83196798360393	-1.31601306392822
H	6.81280356108755	4.25007646734665	-0.48171316840789
H	7.48226671356974	4.42596481662256	-2.14296360858182
H	4.18360289213475	5.92824595350891	-0.98248185975494
H	3.15873381679304	4.54022502713693	-1.48170724654121
H	4.28166115235698	4.37162953118703	-0.09313042320393
H	5.10634752174690	6.11449940138770	-3.36403803114220
H	5.87775967815060	4.69638333153269	-4.15213484372926
H	4.09941158021962	4.72626841941590	-3.87865438594723
H	3.27901555206708	1.26309036945102	-6.41091355035783
H	2.53685179521737	2.61686138561197	-5.49279957238976
H	4.31715257146366	2.35240952726453	-5.43925252551451
H	4.22528875564783	-0.75630140305765	-5.20585180363263
H	5.27707839326776	0.29829897554612	-4.19934382741868
H	4.15663918775410	-0.87609947015549	-3.42083689824880
H	1.66645551897978	-0.40951030325136	-5.17944751930882
H	1.63489459664041	-0.43185552387394	-3.38760540465832
H	0.95764032152236	0.97592827942790	-4.28106244662299
Au	3.06549012905350	-1.50336403044426	-1.13291199695196
Cl	2.88521575146665	-3.82137875675943	-1.37726349414326

Table S13. Cartesian coordinates of the optimized structures for the hypothetical tetra- and pentametallic complexes according to table Table S8.

Coordination on α-P

C	2.00042778068444	1.12661072523987	5.04619997975187
C	2.32505330998598	1.88146986840759	3.74597554104540
C	3.79198352774302	2.35957247255969	3.73068937899146
C	1.37931333483904	3.07027028102772	3.55042471270745
P	2.28594350122092	0.58169467493019	2.34509351740178
P	1.99147704134931	1.82925063263381	0.47242753549241
P	3.35639704460710	0.54028372314759	-0.73770319093409
P	3.07397241373721	1.86009380515578	-2.55100083429032
C	3.02966358586908	0.60726395661912	-3.99170797604176
C	1.61686765982238	-0.00303020020187	-3.93816176043562
P	0.14623713990850	-0.00587693253689	2.07119611288286
C	0.11841285936365	-1.89554026401681	2.07404896289556
C	-1.28785737025925	-2.30809897806745	1.60804437701711
P	0.16103177786647	0.60658129088621	-0.07891203115664
C	-1.20789676453780	1.92331151440493	-0.29020665426967
C	-0.98964133292927	2.41657095984056	-1.73590674375868
C	-2.54824810701405	1.18167850364298	-0.15239371358333
C	-1.13049472887874	3.09941608865327	0.68796018991557
C	1.19672566737967	-2.43931692845007	1.12424365438112
C	0.38957743520309	-2.33092345309586	3.52368625202236
P	5.25818762592072	2.39171996315904	-2.36024897233079
C	5.18730214242584	4.30312212992662	-2.26012188675122
C	4.92666445602943	4.77997812794617	-3.69997456773206
P	5.13680441328101	1.81602604662899	-0.18228203336484
C	6.53246929147485	0.52947723379176	0.02888194755541
C	6.26800977627013	-0.11585404903419	1.40169464010009
C	7.84227048178256	1.33734668929711	0.03646248986976
C	6.56513030880148	-0.53748882275980	-1.07124567976407
C	3.22801588405073	1.44138458118233	-5.26981862534326
C	4.09502895733551	-0.49051677364615	-3.89601430098673
C	4.10031371038206	4.83402155059647	-1.31543725391693
C	6.58079848408004	4.73932366408838	-1.77383238348148
H	2.12884201739228	1.80575199714166	5.91569733653075
H	0.94736215251972	0.77176912499246	5.05416129462266
H	2.66719045617650	0.25207439115900	5.19403526486293
H	1.50786790702637	3.79035799469303	4.38662215493424
H	1.58642331691635	3.60573046911958	2.60202672893255
H	0.31657658394750	2.74880325763373	3.54744817181855
H	3.94159885075450	3.12911378852179	4.51760926301805
H	4.49627712569101	1.52531741894294	3.92598153397440
H	4.06206069253151	2.81340221176738	2.75307146305612
H	0.38437379413145	-3.43934855477600	3.58633996471985
H	1.38355530936965	-1.97935151994423	3.87170807981593
H	-0.38206118821023	-1.93958538372235	4.21810262895346
H	1.16793564053662	-3.54917254129061	1.13381461366716
H	1.03151804806349	-2.10006150712994	0.08159130649747
H	2.21185662213922	-2.11895949899473	1.43432890194682
H	-1.36220342405191	-3.41556887894513	1.58553277101619
H	-2.07335060712122	-1.92080008198258	2.28906950019916
H	-1.49908568815443	-1.93599605623337	0.58350319217937
H	-3.38450505153687	1.87119750690216	-0.39538822872644
H	-2.61298317218521	0.31137463346017	-0.83778021213572
H	-2.70418525225213	0.82318990360145	0.88773256021375
H	-1.92859334622708	3.83501618705964	0.45075951454965
H	-1.28530727187284	2.76699213805439	1.73591678731720
H	-0.15397416980765	3.62063269597946	0.62614903052700
H	-1.74012582406442	3.19823779571077	-1.97993899811478
H	0.02052419379570	2.86032793318270	-1.86684819591213
H	-1.09858321306990	1.59285371274176	-2.47047188308907
H	8.70436489477507	0.66299146181953	0.22893124482349
H	8.01506643674759	1.83059932650601	-0.94341165272373
H	7.83879082721246	2.11970752103810	0.82364067819266
H	7.39704472717479	-1.25097740030954	-0.88400876691953
H	5.62035282008822	-1.11802249981281	-1.09954605204679
H	6.72209543206542	-0.08196860452372	-2.06973309117017
H	7.05095765685369	-0.87198274602987	1.62570306159560
H	6.27491185290385	0.63801010819479	2.21547042278950
H	5.28333211074046	-0.62988158363592	1.42334539593073
H	6.64353691118108	5.84841619366556	-1.74162808325416
H	6.78250116217951	4.36439615264954	-0.74796030359955
H	7.38561573220555	4.36998705332721	-2.44278249014821
H	4.12059232920569	5.94567813069622	-1.30162139547243
H	3.09015872639265	4.51181957270077	-1.63979035471018
H	4.25414069162210	4.47371750089842	-0.27793115108776
H	4.92213703744629	5.89066047348086	-3.73903879490954
H	5.70484871718235	4.41571715054406	-4.40235118936083
H	3.93777022213432	4.43019365807773	-4.06529732664084
H	3.14213256283630	0.79051188392805	-6.16648637849338
H	2.46861464539262	2.24587373444444	-5.35835207344073
H	4.23484242326499	1.90955283305558	-5.29116038322944
H	4.01390630738501	-1.17476609029588	-4.76863526594232
H	5.11705059773034	-0.06096381279690	-3.89075184061474
H	3.96832056868497	-1.09820218469810	-2.97667175320145
H	1.48767591990587	-0.73992675791332	-4.75987542933097
H	1.44125205497790	-0.53161090010571	-2.97684470013554
H	0.83255218407647	0.77375833467027	-4.04608393622269
Au	-1.42954355211388	0.84006390050312	3.46713378281178
Cl	-3.08441081048476	1.60486337031925	4.93026959724738

Coordination on β-P

P	0.12124176635390	0.29063998556102	-0.29781244801520
P	0.11658960115917	0.04828377290277	1.95900161316365
P	2.29667688062546	0.49970352293338	1.85931938997602
P	2.06156788338641	1.45024421695717	-0.15724104150251
P	3.19986470127344	-0.20059486227292	-1.15484924518926
P	2.31231003384638	0.32006920925403	-3.16470491032876
P	4.42252917256635	0.80077241208637	-3.81712937511381
P	4.96242105180946	1.12860815372461	-1.65328475910913
C	6.48667209467900	0.00633128735490	-1.38779034035787
C	2.01372093651444	-1.40116387553146	-3.94755538886034
C	4.21704728464898	2.60363030607584	-4.43659996781911
C	-1.17502545406685	1.66971262377521	-0.56129536150561
C	-0.00595415842489	-1.85130913413754	2.18206106825839
C	2.71059580450706	1.82566534117913	3.12877240836275
Au	3.80129262484170	-1.20981541374753	1.82398378108913
Cl	5.34870357578912	-2.96619134243560	1.87590941348556
C	1.83193127258413	-1.13152985977687	-5.45222566565572
C	3.16179626448276	-2.38984558554576	-3.71276477843325
C	0.71386923851116	-1.93457874118815	-3.32153214458903
H	2.76159557103080	-0.72448123723498	-5.90316390411248
H	1.58950952820779	-2.07869725251328	-5.98051029480394
H	1.00805128610340	-0.41315246304959	-5.64425586316406
H	2.92475309346772	-3.36631731508075	-4.18869949772798
H	4.11085358685158	-2.01792135315109	-4.14886535542242
H	3.32473403821398	-2.57122490537266	-2.63038384520665
H	0.45698778254710	-2.91908293636462	-3.76861585108777
H	0.82030591812780	-2.07037293131082	-2.22575205290085
H	-0.13750040383880	-1.24393075610618	-3.49036426305980
C	2.65348084360063	1.14857830169449	4.50811670210259
C	4.13525252200118	2.29564150498771	2.78353219570008
C	1.70615989263008	2.98191015936303	3.02999835452462
H	2.92316270926627	1.88320513847392	5.29564346335948
H	1.63378390264720	0.77157452956996	4.73130638602853
H	3.36268979842538	0.29757248680735	4.57155006652184
H	4.43731166211899	3.10747744598652	3.47785920126514
H	4.86842851581490	1.46860750001625	2.87551311111392
H	4.19284186483242	2.69433189665197	1.74845942244478
H	1.96469645287068	3.76119228551137	3.77735756690498
H	1.72667393335542	3.45341092458131	2.02640190032233
H	0.67201085306435	2.63934935382598	3.23523935651723
C	0.59105975916474	-2.16314071596637	3.56493704022568
C	-1.52416924187709	-2.12251890955961	2.16390567820822
C	0.68331048513174	-2.67399857010850	1.08717373717545
H	0.42457113713398	-3.23336618489856	3.81115959705699
H	1.68780626569407	-1.98600653175751	3.58031893350842
H	0.12456010947071	-1.55191027750801	4.36522785979463
H	0.56619262958475	-3.75689605155936	1.30607900071589
H	0.24557679338462	-2.47118684118904	0.09002412623515
H	1.77213116266507	-2.45812617181486	1.02912485634288
H	-1.71050885033752	-3.20617023773509	2.32197861754066
H	-2.05508843749170	-1.56218297184612	2.96057860550432
H	-1.97243870324067	-1.84845910004945	1.18561269035283
C	-2.53493908781532	1.00106197029751	-0.29005780311179
C	-0.98359909203763	2.88976393429946	0.34672523629831
C	-1.04054708075440	2.07187763279638	-2.04137387917093
H	-1.77338586877537	3.64384860970322	0.13864862410392
H	-1.05046837455277	2.61325473638356	1.41817265591688
H	-0.00121038630575	3.37437288942618	0.17114406276410
H	-3.35804006955115	1.71637804756067	-0.50309837891188
H	-2.68780713086184	0.10550624652671	-0.92735367516776
H	-2.62871761301860	0.69372884062157	0.77309534592083
H	-1.80327992534591	2.83966470166299	-2.29337803633507
H	-0.03910922694555	2.49980162809351	-2.25524155181491
H	-1.18383104312898	1.20504183707637	-2.71804633061690
C	5.64440258471041	3.16140639212711	-4.57368982532279
C	3.53117933193199	2.49141300840383	-5.80957783561116
C	3.38539473611789	3.48673837495242	-3.49574854995531
H	3.41801260681044	3.49981319895012	-6.26305185163353
H	4.11668406830675	1.86347818883208	-6.51274450990750
H	2.51516828608193	2.05253073234255	-5.71541240887628
H	5.61220699558065	4.19453613534734	-4.98211964506127
H	6.15325995426719	3.20829291706240	-3.58761022072608
H	6.26513041212526	2.54285127993828	-5.25456062479921
H	3.30971532418465	4.51608791816299	-3.90937430292910
H	2.35721754091251	3.08817443404849	-3.37481151322870
H	3.84667103549991	3.55274159042078	-2.48918232238774
C	6.85069610723574	0.18537945587591	0.09785461961547
C	6.23296111425539	-1.46950817096006	-1.71380162356043
C	7.59228324959602	0.57958824406854	-2.29190091957181
H	7.72632632238259	-0.44704659239711	0.35732485090047
H	7.09876754574842	1.24095682096062	0.33195919708056
H	6.01445968355760	-0.12991896625500	0.75809757852579
H	7.16103647538755	-2.05837717514173	-1.54688663159338
H	5.44810581047420	-1.90075414240716	-1.06018582567329
H	5.92942603850826	-1.60051849003996	-2.77183954022912
H	8.54256829062648	0.03050096484809	-2.11768111526217
H	7.33105998158944	0.47182166313022	-3.36577323408073
H	7.77950736749323	1.65410531281912	-2.08474480542399

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