Gold(I) Complexes of P,N Ligands and Their Catalytic Activity

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Gold(I) complexes were readily prepared by reaction of the respective ligands with $(Me_2S)AuCl$ in CH_2Cl_2. Complexes of formula LAuCl {L = diphenyl(2-pyridyl)phosphane (PPh_2Py), (R)-(+)-4-[(2)-(diphenylphosphanyl)-1-naphthyl]-N-[(R)-1-phenylethyl]-1-phthalazinamine (PINAP)} were obtained when a 1:1 molar ratio of ligand to starting gold precursor was used. When a 2:1 ratio of ligand to gold precursor was used with PPh_2Py or MandyPhos as ligands, complexes of the type L_2AuCl were obtained. All complexes were fully characterized, and single-crystal X-ray structures could be determined for four complexes. Chloride ions were removed by reaction with silver salts, such as $AgNTf_2$, AgOTf and $AgBF_4$, for the use of these complexes as catalysts. After the catalytic reaction with alkynes and alcohols in acetonitrile, a unique trinuclear gold(I) complex derived from $[(PPh_2Py)-Au]BF_4$ could be characterized by X-ray structural analysis, showing a mode of catalyst deactivation.

Introduction

The exponential expansion of research interest involving gold in this decade has led to the discovery of many interesting properties and applications of this precious metal. The research on gold covers its various oxidation states (mainly 0, +1, +3, and seldom +2), its coordination chemistry and complexes,[1] the photophysical[2] and catalytic[3] properties of its complexes, and many other areas.[4]

The coordination chemistry of gold(I) complexes, in particular, is well-established. The most striking feature of this d^{10} ion of the group 11 transition metal gold, Au^I, is linear dicoordinate complex formation, whereas Cu^I and Ag^I commonly exist as tetracoordinate species. The favourable linear coordination geometry of gold(I) complexes was assumed to be based on the highest relativistic effect that gold has along the periodic trend, leading to efficient overlapping of s, p and d orbitals.[1c] Tri- and tetracoordinate gold(I) complexes also exist, although they are less common. This may be due to the higher energy required for Au than for Cu and Ag to go from planarity to more distorted angles, as shown by DFT calculations.[5]

In this paper we report the exploration of gold(I) complexes of the P-sp²-N-ligands {diphenyl(2-pyridyl)phosphane (PPh_2Py), (R)-(+)-4-[(2)-(diphenylphosphanyl)-1-naphthyl]-N-[(R)-1-phenylethyl]-1-phthalazinamine (PINAP) and chiral P-sp³-N-ferrocenyl-based diphosphane (MandyPhos)} (Figure 1) and their use as catalysts.
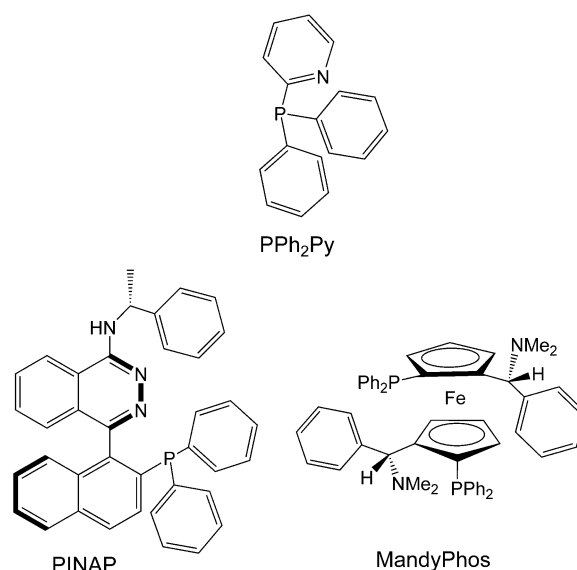
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Figure 1. Phosphane ligands used for the synthesis of Au^I complexes.

Results and Discussion

Simple treatment of a solution of ligand L (L = PPh_2Py or PINAP) with one molar equivalent of $(Me_2S)AuCl$ in dichloromethane gives colourless to pale yellow solutions, from which colourless crystals of [LAuCl] are obtained in 91 or 82% yield, respectively, after slow diffusion of hexane vapour into the solution.

We investigated a single crystal of $[(PPh_2Py)AuCl]$ (**1a**): in the structure determination a decent R value was obtained, but that was dominated by the gold, and because of the overall low quality of the crystal, the aromatic rings had to be treated as fixed hexagons in order to refine them. This

did not allow to distinguish the benzene rings from the pyridine ring, so overall one can only say that the structure is quite similar to that of [Ph₃PAuCl].[6] The structure of the dicoordinate gold(I) complex [(PINAP)AuCl] (**1b**), as determined by an X-ray crystal structure analysis,[7] is shown in Figure 2. Complex **1b** adopts a nearly linear geometry in which the gold atom is coordinated by the phosphorus atom of the phosphane ligand and the chlorido ligand. The P–Au–Cl bond angle is 178.1(8)°. The two aromatic rings, those of the naphthyl and the phthalazinyl groups, lie perpendicular to each other, and they are orthogonal to P–Au–Cl axis. The Au–P and Au–Cl bond lengths of **1b** are 2.23(6) and 2.28(6) Å, respectively, which indicates no unusual structural alteration from many gold(I) complexes known in the literature.[8]
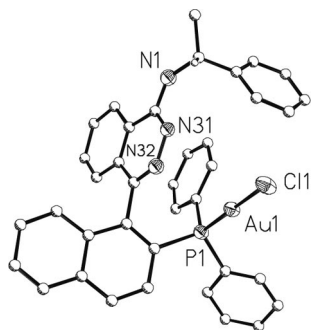

Figure 2. Dicoordinate gold(I) complex [(PINAP)AuCl] (**1b**).

Addition of a twofold excess of ligand (L = PPh₂Py) solution to the (Me₂S)gold(I) chloride in dichloromethane produced a colourless solution, which was concentrated and diffused with hexane. This afforded colourless crystals in 67% yield. The single-crystal X-ray structural analysis of the crystal shows a less common tricoordinate gold(I) complex, [(PPh₂Py)₂AuCl] (**2**) (Figure 3). Although a large family of tricoordinate gold(I) complexes is known, there is only a dozen crystal structures bearing two monodentate phosphane ligands on the gold centre;[9] most of the other known structures contain multidentate ligands or are even substructures of multinuclear gold(I) complexes.[1,10]
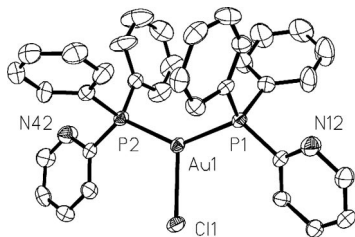

Figure 3. Tricoordinate gold(I) complex [(PPh₂Py)₂AuCl] (**2**).

Compound **2** shows a trigonal planar geometry consisting of one gold, two phosphorus and one chlorine atoms. The two phosphane ligands coordinate to the Au^I centre with an Au(1)–P(1) distance of 2.32(2) Å and an Au(1)–P(2) distance of 2.30(5) Å. The third coordination site is occupied by a chlorido ligand with an Au(1)–Cl(1) bond length of 2.54(4) Å. The bond angle of P(2)–Au(1)–

P(1) is 137.3(9)°. The P(2)–Au(1)–Cl(1) and P(1)–Au(1)–Cl(1) bond angles are 114.5(1) and 107.7(1)°, respectively. These physical features of complex **2** lie midway between two other very similar structures made of phosphane ligands.[9a,9c] A summary of important interatomic distances and angles of these chloridobis(phosphanyl)gold(I) complexes is given in Table 1.

Table 1. Summary of important interatomic distances [Å] and angles [°].

| Compound	Au–X	Au–P(1)	Au–P(2)	P(1)–Au–P(2)
(Ph₃P)₂AuCl	2.500(4)	2.323(4)	2.339(4)	132.1(1)
(PhCy₂P)₂AuCl	2.744(2)	2.324(1)	2.300(1)	158.24(5)

The most intriguing aspect of **2** is the comparison of angle P(2)–Au(1)–P(1) (∠ PAuP) with that of similar complexes. This angle lies closer to that of [(Ph₃P)₂AuCl], showing a nearly trigonal planar geometry of the complex. The slightly larger ∠ PAuP of **2** causes a tighter bonding between Au^I and phosphorus atoms of the ligands. A slightly longer Au–Cl bond was also observed for **2** relative to [(Ph₃P)₂AuCl]. On the other hand, [(PhCy₂P)₂AuCl] shows a distorted nature with a nearly linear arrangement between the two phosphorus atoms and the gold atom (∠ PAuP 158.2°). Nonetheless, the Au–P distances of [(PhCy₂P)₂AuCl] are comparable to **2**, the most striking difference being observed in the Au–Cl distance [2.74(4) Å].

The approach to obtain **2** was also used to synthesize tricoordinate gold(I) complexes containing a chiral phosphane ligand, specifically by using the MandyPhos ligand (Figure 4). The resultant crystal was obtained as a tricoordinate polymer of formula [{(MandyPhos)AuCl}ₙ] (**3**). Only a few examples[11] exist in the literature for polymeric gold(I) complexes, but compound **3** shown here is the first evidence of a polymeric tricoordinate gold(I) complex containing a chiral phosphane ligand.

The structure of **3** comprises a polymeric chain structure involving bridging ferrocenylphosphane units linking trigonal Au–Cl groups. Although a 1:1 molar ratio of ligand to gold was observed, the two phosphorus atoms of one MandyPhos ligand are coordinated to different Au^I ions. In other words, the MandyPhos ligand acts as a bridging ligand between two Au^I ions. A similar polymeric structure was obtained by Houlton et al. by using the diphosphane ligand.[11c] Table 2 shows the selected bond lengths and angles of complex **3** relative to the most structurally similar complex, [{(μ-dppf)AuCl}ₙ] [dppf = 1,1′-bis(diphenylphosphanyl)ferrocene].[11c] The most noticeable feature of the two structures is that the P–Au–P angle is smaller for **3**, which is reflected in longer Au–P bond lengths.

The Au–P bond lengths of **3** throughout the polymer structure range from 2.329(5) to 2.347(5) Å. The slightly longer Au–P bond lengths of **3** relative to Au–P bond lengths of other gold(I) complexes could be rationalized as by the explanation that the metallocene unit pulls the electron density away from phosphorus atom for better binding with Au^I. However, the Au–Cl bond lengths of **3** show no significant variation.
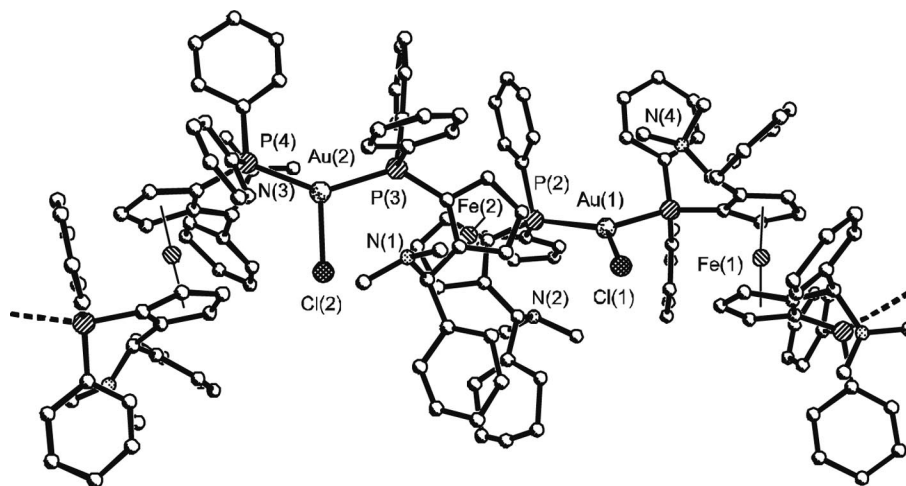
Figure 4. Tricoordinate gold(I) complex [{(MandyPhos)AuCl}$_n$] (**3**).

Table 2. Selected bond lengths [Å] and angles [°] of **3**.

	[{(MandyPhos)AuCl}$_n$]	[{(μ-dppf)AuCl}$_n$]
Au(1)–P(1)	2.336(5)	2.315(2)
Au(1)–P(2)	2.343(5)	
Au(1)–Cl(1)	2.572(6)	2.550(3)
Au(2)–P(4)	2.329(5)	
Au(2)–P(3)	2.347(5)	
Au(2)–Cl(2)	2.590(6)	
P(1)–Au(1)–P(2)	133.01(19)	136.5(1)
P(1)–Au(1)–Cl(1)	116.00(18)	112.7(1)
P(2)–Au(1)–Cl(1)	110.98(18)	110.8(1)
P(4)–Au(1)–P(3)	138.0(2)	
P(4)–Au(2)–Cl(2)	113.77(18)	
P(3)–Au(2)–Cl(2)	108.22(19)	

Table 3. Catalyzed addition of water to 1-pentyne in acetonitrile, delivering 2-pentanone.

Entry	Catalyst	Amount [mol-%]	T [°C]	% Yield[a]
1	[AuPPh$_2$Py]NTf$_2$	5	50	100
2	[AuPPh$_2$Py]OTf	5	70	100
3	[AuPPh$_2$Py]OTf	3	70	67
4	[AuPPh$_2$Py]OTf	2	70	65
5	[AuPPh$_2$Py]OTf	1	70	61
6	[AuPPh$_2$Py]BF$_4$	5	50	100
7	[AuPPh$_2$Py]BF$_4$	3	50	85
8	[AuPPh$_2$Py]BF$_4$	2	70	55
9	[AuPPh$_2$Py]BF$_4$	1	50	40
10	[AuPPh$_2$Py]BF$_4$	0.5	50	23

[a] Against an internal standard of the nonvolatile *tert*-butylacet-amide.

When an equimolar amount of a silver salt of various anions, BF_4^-, OTf^- and NTf_2^-, was added to a solution containing gold(I) complexes in dichloromethane, immediate precipitation of AgCl was observed. The solution was filtered, and the solvent was removed. The attempts to crystallize the complex after chloride ion removal only resulted in oily material.

Having prepared these nearly linear and distorted trigonal planar tricoordinate chloridogold(I) complexes and having removed the chloride ions from these complexes, we tested them for the simple gold-catalyzed addition of water to 1-pentyne. This addition follows the normal Markovnikov regioselectivity, and the only product observed is 2-pentanone (Table 3). The NTf_2^- salt derived from **1a** leads to a good conversion to the product at 50 °C (entry 1). The corresponding triflate needs 70 °C to reach completion (entry 2), reducing the amount of catalyst also reduces the yield (entries 3–5), no full conversion is observed. The BF_4^- salt operates at 50 °C, again the yield drops significantly with the catalyst amount (entries 6–10). Overall, the turnover numbers are in no way outstanding (between 5 and 20),[3] but they raise the interesting question of the modes of catalyst deactivation.

Fortunately, the unprecedented outcome of one of the catalytic reactions is the insight on how the activated gold(I) catalyst with the PPh$_2$Py ligand became inactive during the reaction. On one hand, a gold mirror deposited onto the glass surface was observed in many of the reactions run with [(PPh$_2$Py)Au]BF$_4$ as catalyst. On the other hand, in some cases, red crystalline material aggregated on the glass surface after the reaction. Single-crystal X-ray structural analysis of the deposited crystal on the glass shows formation of the unique trinuclear gold(I) aggregate **4**, which is the deactivated catalyst (Figure 5).

Structure **4** crystallizes as a unit cell with three BF_4^- counterions statistically distributed over four sites in the lattice. Each Au(1), Au(2) and Au(3) atom of the cluster is still coordinated to the P atom of the initial PPh$_2$Py ligand. The Au–P distances are 2.238(2), 2.237(2) and 2.239(2) Å for Au(1), Au(2) and Au(3), respectively. These bond lengths are slightly longer than those in **1a**. Each Au atom is also coordinated to the nitrogen atom of the pyridine group of the PPh$_2$Py ligand of the adjacent gold complex, thus completing the homonuclear gold complex. The Au–N distances are measured to be 2.100(7), 2.103(8) and 2.115(8) Å for Au(1)–N(3), Au(2)–N(1) and Au(3)–N(2), respectively.
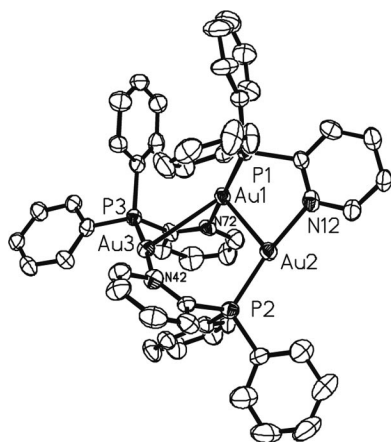
Figure 5. Deactivated gold(I) trimer observed after a catalytic reaction (**4**).

These bond lengths are comparable to other known Au–N distances.[12] The Au(2) atom of the cluster formed a tetra-coordinate center, coordinating to Au(1) and Au(3) in addition to Au–P and Au–N bonding. The Au(2)–Au(1) and Au(2)–Au(3) bond lengths are measured to be 3.048(3) and 3.226(9) Å, respectively. Once again, these bond lengths lie within the range that was observed in the literature.[13] It appeared that [(PPh$_2$Py)Au]$^+$ in the reaction solution becomes deactivated by coordinating with the nitrogen atom of the ligand of the adjacent complex. Table 4 lists the high-lighted parameters (bond lengths [Å] and bond angles [°]) of the crystal.

Table 4. Selected bond lengths [Å] and bond angles [°] of **4**.

	[(PPh$_2$Py)$_3$Au$_3$]$^{3+}$
Au(1)–N(3)	2.100(7)
Au(1)–P(1)	2.238(2)
Au(1)–Au(2)	3.0483(6)
Au(1)–Au(3)	3.2269(7)
Au(2)–N(1)	2.103(8)
Au(2)–P(2)	2.237(2)
Au(3)–N(2)	2.115(8)
Au(3)–P(3)	2.239(2)
N(3)–Au(1)–P(1)	168.3(2)
N(3)–Au(1)–Au(2)	111.8(2)
P(1)–Au(1)–Au(2)	75.91(7)
N(3)–Au(1)–Au(3)	80.3(2)
P(1)–Au(1)–Au(3)	110.29(7)
Au(2)–Au(1)–Au(3)	80.478(14)
N(1)–Au(2)–P(2)	171.9(2)
N(1)–Au(2)–Au(1)	82.3(2)
P(2)–Au(2)–Au(1)	105.69(7)
N(2)–Au(3)–P(3)	175.3(2)
N(2)–Au(3)–Au(1)	114.3(2)
P(3)–Au(3)–Au(1)	68.81(6)

Conclusions

We have synthesized and characterized an array of gold(I) complexes that contain strikingly different structural properties. Some of the complexes shown here have catalytic activities, which, for example, become deactivated

by forming unique gold aggregates. Photophysical properties of these complexes may be one interesting aspect for future study.

Experimental Section

General: All procedures were carried out under a dry argon atmosphere using Schlenk and vacuum-line techniques. All solvents were dried and purified by an MBRAUN Solvents Purification System (SPS-800). All common reagents were used as purchased without further purification. The starting gold complex, [(Me$_2$S)AuCl], was obtained from Aldrich Chemicals and used as received.

All NMR spectra were recorded with a Bruker Avance 200 (200.2 MHz for ^{1}H, 50.3 MHz for ^{13}C, and 80.02 MHz for ^{31}P NMR spectra) instrument. ^{1}H and ^{13}C NMR chemical shifts are reported in ppm relative to the ^{1}H and ^{13}C residues of the deuterated solvents. ^{31}P NMR chemical shifts are reported in ppm relative to an 85% H$_3$PO$_4$ external standard solution. ESI mass spectra were recorded with a Finnigan TSQ700 Tripelquadrupole mass spectrometer. Gas chromatography–mass spectrometry (GC–MS) was performed with an Agilent 6890N gas chromatograph fitted with a 7683B Series mass selective detector.

X-ray Structural Determinations: Frames corresponding to a sphere of data were collected by using 0.3° ω scans with a SMART CCD area detector: Mo-K_α, λ = 0.71073 Å radiation. Intensities were corrected for Lorentz and polarization effects, and an empirical absorption correction was applied by using the SADABS[14] program based on the Laue symmetry of the reciprocal space. Structure solution and refinement was carried out with the SHELXL-97[14] program system.

General Procedure for the Synthesis of Gold(I) Chloride Complexes: All procedures were carried out under an argon atmosphere. To a stirred solution of [(Me$_2$S)AuCl] was added by cannula in the dark the ligand solution in CH$_2$Cl$_2$. The reaction solution was stirred for at least 2 h at room temperature. The resulting solution was then concentrated under vacuum, and hexane was layered on the concentrated solution to precipitate white powders. The product precipitate was filtered and recrystallized with CH$_2$Cl$_2$/hexane.

[Diphenyl(2-pyridyl)phosphane]gold(I) Chloride [(PPh$_2$Py)AuCl] (1a): A solution of diphenyl(2-pyridyl)phosphane (489 mg, 1.90 mmol) in CH$_2$Cl$_2$ (50 mL) was added to a stirred solution of [(Me$_2$S)AuCl] (547 mg, 1.90 mmol) in CH$_2$Cl$_2$ (50 mL) at room temperature under argon. The mixture was stirred for 2 h, then it was concentrated under reduced pressure, and hexane was added to precipitate out the product as a white powder; yield 867 mg, 92%. ^{1}H NMR (200.2 MHz, CD$_2$Cl$_2$, 298 K): δ = 7.2–7.9 (m, 13 H, Ph, Py), 8.75 [d, J(H,H) = 4.6 Hz, 1 H, Py] ppm. ^{13}C NMR (50.3 MHz, CD$_2$Cl$_2$, 298 K): δ = 125.9 (1 C), 128.3 (1 C), 129.4 (4 C), 131.3 (1 C), 132.2 (1 C), 132.4 (2 C), 134.9 (4 C), 137.1 (2 C), 151.7 (1 C) ppm. ^{31}P NMR (81.02 MHz, CD$_2$Cl$_2$, 298 K): δ = 32.4 (s) ppm. FAB+: calcd. m/z = 460 for [(PPh$_2$Py)Au]$^+$ (C$_{17}$H$_{14}$AuNP); found m/z (%) = 460 (100). C$_{17}$H$_{14}$AuClP (495.69): calcd. C 41.19, H 2.85, N 2.83; found C 40.57, H 2.86, N 2.76. IR (KBr): $\tilde{\nu}$ = 513 (s), 545 (s), 692 (s), 727 (m), 749 (s), 770 (m), 988 (m), 998 (w), 1102 (s), 1183 (w), 1422 (m), 1436 (s), 1449 (w), 1480 (m), 1571 (m), 1628 (m), 3052 (m) cm^{-1}.

{(R)-(+)-4-[2-(Diphenylphosphanyl)-1-naphthyl]-N-[(R)-1-phenylethyl]-1-phthalazinamine}gold(I) Chloride [(PINAP)AuCl] (1b): To a stirred solution of [(Me$_2$S)AuCl] (39.3 mg, 133 µmol) in CH$_2$Cl$_2$ (20 mL) was added a solution of (R)-(+)-4-[2-(diphenylphos-

phanyl)-1-naphthalenyl]-*N*-[(*R*)-1-phenylethyl]-1-phthalazinamine (74.7 mg, 134 µmol) in CH$_2$Cl$_2$ (20 mL) at room temperature under argon. Work-up as described for **1a**; yield 85.9 mg, 82%. ^{1}H NMR (200.2 MHz, CD$_2$Cl$_2$, 298 K): δ = 1.65 [d, *J*(H,H) = 6.5 Hz, 3 H, CH$_3$], 5.45 (m, ^{1}H NH), 5.87 (m, 1 H, CH), 6.90–7.90 (m, 25 H, phenyl, phthalizine and naphthalene groups) ppm. ^{13}C NMR (50.3 MHz, CD$_2$Cl$_2$, 298 K): δ = 22.7 (CH$_3$), 51.1 (CH), 118.0 (C), 120.9 (CH), 126.9 (CH), 127.9 (CH), 127.3 (CH), 127.5 (CH), 128.4 (CH), 128.5 (CH), 128. 6 (CH), 128.6 (CH), 128.63 (CH), 128.7 (CH), 128.7 (CH), 129.0 (CH), 130.1 (CH), 131.3 (CH), 131.4 (CH), 133.5 (two separate signals, CH), 133.6 (C), 133.7 (CH), 133.9 (CH), 134.0 (C), 134.1 (CH), 136.3 (C), 136.6 (C), 137.4 (C), 137.6 (C), 137.9 (C), 138.2 (C), 141.9 (C), 142.5 (C), 145.0 (C), 152.8 (C), 152.9 (C), 153.0 (C) ppm. ^{31}P NMR (81.0 MHz, CD$_2$Cl$_2$, 298 K): δ = 28.72 (s) ppm. MS (ESI+): calcd. for [AuLCl + H]$^+$ (C$_{38}$H$_{31}$AuClN$_3$P) 792.153; found 792.1605. C$_{38}$H$_{30}$AuClN$_3$P (792.06): calcd. C 57.70, H 3.67, N 5.31; found C 58.62, H 4.23, N 5.24. IR (KBr): $\tilde{\nu}$ = 505 (w), 520 (w), 540 (m), 664 (w), 693 (s), 749 (m), 1099 (m), 1129 (w), 1365 (m), 1394 (w), 1437 (s), 1485 (m), 1507 (s), 1551 (w), 1579 (w), 1629 (m, broad), 2923 (m), 3057 (w) cm^{-1}.

Single-Crystal X-ray Structure Determination for 1b: Empirical formula: C$_{40}$H$_{34}$AuCl$_5$N$_3$P, formula weight: 961.89 g mol^{-1}, *T* = 200(2) K, λ = 0.71073 Å, crystal system: monoclinic, space group: *P*2$_1$, *Z* = 2, unit cell dimensions: *a* = 10.6441(1) Å; α = 90°; *b* = 9.2667(2) Å; β = 97.551(1)°; *c* = 19.3538(1) Å; γ = 90°; *V* = 1892.42(5) Å^3; *d*(calculated) = 1.69 g/cm^3; absorption coefficient: 4.32 mm^{-1}, crystal shape: platelet, crystal size: 0.46 × 0.12 × 0.04 mm^3, crystal colour: colourless, θ range for data collection: 1.9 to 24.1°, limiting indices: –12 < *h* < 12, –10 < *k* < 10, –22 < *l* < 22; reflections collected: 14205, independent reflections: 5935 [*R*(int) = 0.0925], observed reflections: 4480 [*I* > 2σ(*I*)], absorption correction: semiempirical from equivalents, max./min. transmission: 0.85/0.24, refinement method: full-matrix least-squares on *F*^{2}, data/restraints/parameters: 5935/8/238, goodness-of-fit on *F*^{2} = 1.05, final *R* indices [*I* > 2σ(*I*)] = R1 = 0.075, *wR2* = 0.159; absolute structure parameter: 0.066(17), largest diff. peak and hole: 3.16 and –2.27 e Å^{-3}.

Bis[diphenyl(2-pyridyl)phosphane]gold(I) Chloride [(PPh$_2$Py)$_2$AuCl] (2): To a stirred solution of (Me$_2$S)AuCl (59.0 mg, 20.0 mmol) in CH$_2$Cl$_2$ (10 mL) was added a solution of diphenyl(2-pyridyl)phosphane (105 mg, 40.0 mmol) in CH$_2$Cl$_2$ (10 mL) at room temperature under argon. The solution mixture was stirred for 2 h. The solution was concentrated under reduced pressure, and hexane was added to precipitate the product out as a white powder; yield 102 mg, 67%. ^{1}H NMR (200.2 MHz, CD$_2$Cl$_2$, 298 K): δ = 7.15–7.70 (m, 26 H, Ph, Py), 8.65 [d, *J*(C,H1) = 4.6 Hz, 2 H, Py] ppm. ^{13}C NMR (50.3 MHz, CD$_2$Cl$_2$, 298 K): δ = 124.7 (2 C), 129.1 (8 C), 129.3 (2 C), 130.4 (2 C), 131.2 (4 C), 134.5 (8 C), 134.9 (2 C), 136.7 (2 C), 151.0 (2 C) ppm. ^{31}P NMR (81.0 MHz, CD$_2$Cl$_2$, 298 K): δ = 27.98 (s) ppm. MS (ESI+): calcd. for [Au(PPh$_2$Py)$_2$]$^+$ (C$_{34}$H$_{28}$AuN$_2$P$_2$) 723.1374 ; found 723.1374. C$_{34}$H$_{28}$AuClN$_2$P$_2$ (758.97): calcd. C 53.81, H 3.72, N 3.69; found C 53.41, H 3.68, N 3.65. IR (KBr): $\tilde{\nu}$ = 518 (s), 544 (w), 618 (w), 694 (s), 725 (w), 744 (s), 770 (w), 988 (w), 1027 (w), 1098 (m), 1156 (w), 1185 (w), 1422 (s), 1435 (m), 1449 (m), 1571 (s), 1631 (broad s), 3050 (m) cm^{-1}.

Single-Crystal X-ray Structure Determination for 2: Empirical formula: C$_{34}$H$_{28}$AuClN$_2$P$_2$, formula weight 758.95 g mol^{-1}, colourless, *T* = 200 K, λ = 0.71073 Å, crystal system: triclinic, space group: *P*$\bar{1}$, unit cell dimensions: *a* = 10.7531 (13) Å; α = 113.516(3)°; *b* = 11.6519(14) Å; β = 94.768(3)°; *c* = 14.2282(18); γ = 109.098(3)°; *V* = 1497.0(3) Å^3; calculated density: 1.684 Mg/m^3; absorption coeffi-

cient: 5.136 mm^{-1}, *F*(000) = 744, crystal size: 0.31 × 0.05 × 0.01 mm, θ range for data collection: 1.61–24.71°, limiting indices: –12/12, –13/13, –16/16, 11994 reflections collected: 5095 unique [*R*(int) = 0.0469], completeness to θ = 24.71:99.7%, absorption correction: semiempirical from equivalents, max./min. transmission: +0.9504 and 0.2989, refinement method: full-matrix least-squares on *F*^{2}, data/restraints/parameters: 5095/0/361, goodness of fit on *F*^{2} = 1.021, final *R* indices [*I* > 2σ(*I*)]: R1 = 0.0456, *wR2* = 0.0974, *R* indices (all data): R1 = 0.0552, *wR2* = 0.1012, largest diff. peak and hole: 1.272 and –1.953 e A^{-3}.

(MandyPhos)gold(I) Chloride [{(MandyPhos)AuCl}$_n$] (3): To a stirred solution of [(Me$_2$S)AuCl] (3.00 mg, 10.0 µmol) in CH$_2$Cl$_2$ (1.0 mL) was added a solution of MandyPhos (16.0 mg, 20.0 µmol) in CH$_2$Cl$_2$ (1.0 mL) at room temperature under argon. Work-up as described for **1a**; yield 10.9 mg (61%). ^{1}H NMR (200.2 MHz, CD$_2$Cl$_2$, 298 K): δ = 1.30 (s, 12 H, NCH$_3$), 3.21 (br. s, 2 H, NCH), 3.52 (br. s, 2 H, CH), 4.48 (br. s, 2 H, ferrocene), 4.59 (br. s, 2 H, ferrocene), 6.90–7.25 (m, 30 H, Ph) ppm. ^{13}C NMR (50.3 MHz, CD$_2$Cl$_2$, 298 K): δ = 40.5 (4 C, CH$_3$), 67.4 (2 C), 71.2 (2 C, Cp), 72.5 (2 C, Cp) 73.3 (2 C, Cp), 74.9 (2 C, Cp), 96.9 (2 C, Cp), 126.1 (2 C, Ph), 126.8 (2 C, Ph), 127.2 (2 C, Ph), 127.4 (4 C, Ph) 128.1 (12 C, Ph), 128.5 (2 C, Ph), 129.1 (4 C, Ph) 131.7 (2 C, Ph), 134.0 (2 C, Ph), 135.9 (2 C, Ph), 137.7 (2 C, Ph) ppm. ^{31}P NMR (81.0 MHz, CD$_2$Cl$_2$, 298 K): δ = –9.69 to –11.31 (broad) ppm. MS (ESI+): calcd. for [AuL]$^+$ 1017.26207; found 1017.25054. C$_{52}$H$_{50}$AuClFeN$_2$P$_2$ (1053.18): calcd. C 59.14, H 4.9, N 2.65; found C 59.93, H 4.96, N 2.62.

Single-Crystal X-ray Structure Determination for 3: Empirical formula: C$_{52.50}$H$_{51}$AuCl$_2$FeN$_2$P$_2$; formula weight: 1095.61 g mol^{-1}, *T* = 200(2) K, λ = 0.71073 Å, crystal system: orthorhombic, space group: *P*2(1)2(1)2(1), unit cell dimensions: *a* = 14.5722(3) Å; α = 90°, *b* = 35.3453(8) Å; β = 90°, *c* = 22.9088(5) Å; γ = 90°, *V* = 11799.4(4) A^3, *Z* = 8, calculated density: 1.233 Mg/m^3, absorption coefficient: 2.905 mm^{-1}, *F*(000) = 4392, crystal size: 0.36 × 0.33 × 0.24 mm, θ range for data collection: 1.06 to 25.71°, limiting indices: –17 ≤ *h* ≤ 17, –42 ≤ *k* ≤ 43, –27 ≤ *l* ≤ 27, reflections collected/unique: 97175/22432 [*R*(int) = 0.1365], completeness to θ = 25.71 (99.9%), absorption correction: semiempirical from equivalents, max./min. transmission: 0.5424 and 0.4211, refinement method: full-matrix least-squares on *F*^{2}, data/restraints/parameters: 22432/0/1063, goodness-of-fit on *F*^{2} = 1.081, final *R* indices [*I* > 2σ(*I*)]: R1 = 0.1017, *wR2* = 0.2671, *R* indices (all data): R1 = 0.1564, *wR2* = 0.3215, absolute structure parameter: 0.881(14), largest diff. peak and hole: 4.549 and –3.643 e A^{-3}.

General Procedure for Chloride Ion Removal from (L)$_n$AuCl Complexes by Using Silver(I) Salts: To a stirred solution of [LAuCl] in CH$_2$Cl$_2$ was added an equimolar amount of silver salt bearing weakly coordinating counter anions, such as BF$_4^-$, OTf$^-$ and NTf$_2^-$. Immediate precipitation of AgCl was observed in all cases. The solution was stirred for 1 h, filtered, and the filtrate was concentrated to dryness. The resulting solid ranged in colour from greyish white to purplish red.

Chloride Ion Removal from [(PPh$_2$Py)AuCl] by Using AgNTf$_2$: Removal of Cl$^-$ resulted in a white precipitate in quantitative yield. ^{1}H NMR (200.15 MHz, CD$_2$Cl$_2$, 298 K): δ = 7.22–7.61 (m, 11 H ppm. Ph, Py), 7.89 (br. s, 1 H, Py), 8.09 [t, *J*(H,H) = 8.0 Hz, 1 H, Py], 9.08 [d, *J*(H,H) = 4.5 Hz, 1 H, Py]. ^{31}P NMR (81.02 MHz, CD$_3$CN, 298 K): δ = 30.4 (s, PPh) ppm. IR (KBr): $\tilde{\nu}$ = 512 (s), 542 (s), 571 (s), 600 (s), 653 (m), 692 (s), 742 (m), 792 (w), 997 (w), 1029 (m), 1058 (s), 1101 (m), 1140 (s), 1197 (s), 1350 (s), 1438 (m), 1592 (w), 1624 (w) cm^{-1}.

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Chloride Ion Removal from [(PPh₂Py)AuCl] by Using AgOTf: ¹H NMR (200.15 MHz, CD₂Cl₂, 298 K): δ = 7.15 (m, 1 H, Py), 7.25–7.60 (m, 10 H, Ph, Py), 8.03 (m, 1 H, Py), 8.23 (m, 1 H, Py), 9.22 [d, *J*(H,H) = 4.8 Hz, 1 H, Py] ppm. ³¹P NMR (81.02 MHz, CD₃CN, 298 K): δ = 29.9 (s, P*Ph*) ppm. IR (KBr): ṽ = 513 (s), 543 (s), 573 (s), 638 (s), 693 (s), 714 (s), 727 (m), 752 (s), 997 (w), 1031 (s), 1101 (s), 1161 (s), 1260 (s), 1424 (w), 1437 (s), 1481 (w), 1572 (w), 1591 (w), 1625 (w) cm⁻¹.

Chloride Ion Removal from [(PPh₂Py)AuCl] by Using AgBF₄: ¹H NMR (200.2 MHz, CD₂Cl₂, 298 K): δ = 7.18–7.67 (m, 13 H, Ph, Py), 8.71 [d, *J*(H,H) = 5.3 Hz, 1 H, Py] ppm. ¹³C NMR (50.3 MHz, CD₂Cl₂, 298 K): δ = 123.4 (1 C), 124.9 (1 C), 128.8 (1 C), 130.5 (4 C), 133.0 (2 C), 134.6 (2 C), 135.1 (4 C), 142.5 (1 C), 155.8 (1 C) ppm. ³¹P NMR (81.02 MHz, CD₂Cl₂, 298 K): δ = 30.1 (s, P*Ph*) ppm. C₁₇H₁₄AuBF₄NP (547.04): calcd. C 37.32, H 2.58, N 2.56; found C 36.94, H 2.80, N 2.58. IR (KBr): ṽ = 501 (m), 512 (m), 543 (s), 692 (m), 714 (m), 727 (w), 750 (m), 997 (m), 1101 (s), 1123 (s), 1185 (w), 1423 (w), 1427 (s), 1481 (w), 1571 (w), 1591 (w), 1628 (w), 3056 (w) cm⁻¹.

Chloride Ion Removal from [(PPh₂Py)₂AuCl] by Using AgNTf₂: ¹H NMR (200.2 MHz, CD₂Cl₂, 298 K): δ = 7.25–7.65 (m, 24 H, Ph), 7.84 (m, 2 H, Py), 8.79 [d, *J*(H,H) = 4.0 Hz, 2 H, Py] ppm. ¹³C NMR (50.3 MHz, CD₂Cl₂, 298 K): δ = 122.1 (2 C), 123.4 (2 C), 126.5 (2 C), 130.2 (8 C), 132.7 (4 C), 133.3 (4 C), 134.7 (8 C), 141.3 (2 C), 152.0 (2 C) ppm. ³¹P NMR (81.02 MHz, CD₂Cl₂, 298 K): δ = 44.2 (s, P*Ph*) ppm. MS (ESI+): calcd. for [Au(PPh₂Py)₂]⁺ (C₃₄H₂₈AuN₂P₂) 723.139; found 723.1374. IR (KBr): ṽ = 512 (s), 542 (s), 571 (s), 600 (s), 653 (m), 692 (s), 742 (m), 792 (w), 997 (w), 1029 (m), 1058 (s), 1101 (m), 1140 (s), 1197 (s), 1350 (s), 1438 (m), 1592 (w), 1624 (w) cm⁻¹.

Chloride Ion Removal from [(PINAP)AuCl] by Using AgBF₄: Removal of Cl⁻ resulted in a white precipitate; yield 81.6%. ¹H NMR (200.2 MHz, CD₂Cl₂, 298 K): δ = 1.70 [d, *J*(H,H) = 6.8 Hz, 3 H], 6.16 (m, 2 H), 6.60–8.20 (m, phenyl, phthalizine and naphthalene groups) ppm. ¹³C NMR (50.3 MHz, CD₂Cl₂, 298 K): δ = 20.2 (CH₃), 50.0 (CH), 117.8 (C), 120.5 (CH), 126.1 (CH), 127.2 (CH), 126.9 (CH), 127.0 (CH), 127.7 (two separate signals), 127.9 (two separate signals, CH), 128.0 (CH), 128.1 (two separate signals, CH), 128.5 (CH), 129.9 (CH), 130.3 (CH), 130.4 (two separate signals, CH), 132.8 (CH), 132.5 (C), 132.7 (CH), 132.9 (CH), 133.6 (C), 133.9 (CH), 135.1 (C), 135.2 (C), 136.7 (C), 136.8 (C), 137.3 (C), 137.9 (C), 141.1 (C), 141.7 (C), 144.2 (C), 150.9 (C), 151.1 (C), 152.3 (C) ppm. ³¹P NMR (81.02 MHz, CD₃CN, 298 K): δ = 30.61 (s) ppm. IR (KBr): ṽ = 505 (w), 519 (w), 535 (w), 665 (w), 693 (s), 750 (m), 998 (w), 1084 (s), 1124 (s), 1373 (w), 1395 (w), 1437 (s), 1508 (s), 1559 (w), 1581 (w), 3386–3588 (m, broad) cm⁻¹.

[Diphenyl(2-pyridyl)phosphane]gold(I) Trimer (4): The gold(I) trimer was collected as deactivated catalyst upon an attempted addition of *tert*-butyl alcohol to pentyne. A catalytic amount (5 mol-%) of [biphenyl(2-pyridyl)phosphane]gold(I) tetrafluoroborate was dissolved in a small amount of deuterated acetonitrile and added to the bulk solution mixture in a J. Young NMR tube containing the substrates *tert*-butyl alcohol and 1-pentyne under argon. The reaction was carried out at 50 °C and followed by periodical proton NMR spectroscopic measurements. Small crystals formed in the NMR tube, which were analyzed by single-crystal X-ray diffraction. C₅₃H₄₅Au₃B₄F₁₆N₄P₃ (1768.98): calcd. C 37.32, H 2.58, N 2.56; found C 37.02, H 2.66, N 2.61.

Single X-ray Crystal Structure Determination for 4: Empirical formula: C₅₃H₄₅Au₃B₄F₁₆N₄P₃ formula weight: 1768.98 g mol⁻¹, *T* = 200(2) K, λ = 0.71073 Å, crystal system: triclinic, space group: *P*1̄, unit cell dimensions: *a* = 10.7435(18) Å, α = 98.753(3)°, β = 12.883(2) Å, β = 90.277(3)°, *c* = 24.540(4) Å, γ = 109.837(2)°, *V* = 3151.9(9) Å³, *Z* = 2, calculated density: 1.864 Mg/m³, absorption coefficient: 7.126 mm⁻¹, *F*(000) = 1674, crystal size: 0.22 × 0.14 × 0.14 mm, θ range for data collection: 0.84 to 28.40°, limiting indices: –14 ≤ *h* ≤ 14, –17 ≤ *k* ≤ 17, –32 ≤ *l* ≤ 32, reflections collected/unique: 32034/15485 [*R*(int) = 0.0717], completeness to θ = 28.40 97.8%, absorption correction: semiempirical from equivalents, max. and min. transmission: 0.4353 and 0.3032, refinement method: full-matrix least-squares on *F*², data/restraints/parameters: 15485/0/749, goodness-of-fit on *F*² = 1.004, final *R* indices [*I* > 2σ(*I*)] R1 = 0.0564, *w*R2 = 0.1413, *R* indices (all data): R1 = 0.0918; *w*R2 = 0.1617, largest diff. peak and hole: 2.073 and –1.747 e A⁻³.

Standard Procedure for Auᴵ-Catalyzed Addition of Water: All experiments were performed by using 5 mol-%, with regard to pentyne, activated Auᴵ complex of various counterions such as BF₄⁻, OTf⁻ and NTf₂⁻. The degassed and argon-purged pentyne, water (10 equiv.) and *tert*-butylacetamide as an internal standard were added to sealed NMR tubes with a disposable syringe under an argon atmosphere. A small amount (100 µL) of deuterated acetonitrile was added to the solution, and the proton NMR spectrum at room temperature was measured as the initial spectrum of the experiment. A catalytic amount of activated Auᴵ complex dissolved in a small amount of deuterated acetonitrile was then added to the solution. The NMR solution tube was submerged in an oil bath preheated to 50 °C, and the solution progress was monitored every hour by NMR spectroscopy until no changes were observed after 48 h.

Product solutions at room temperature were filtered to remove deactivated gold catalyst precipitates prior to the analysis. Product solution (100 µL) diluted in acetonitrile was used for the analysis. Percentage yields were calculated on the basis of the internal standard concentration.

Vacuum fractional distillation with Kugelrohr apparatus was performed to isolate the products of the reaction. In general, a small round-bottomed flask containing the product solution was slowly heated under partial vacuum to fractionally collect the products with different boiling points. The isolated products were further analyzed by proton and carbon NMR spectroscopy.

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