Available online at www.sciencedirect.com
SCIENCE DIRECT
Inorganic Chemistry Communications 9 (2006) 355–359
INORGANIC CHEMISTRY COMMUNICATIONS
www.elsevier.com/locate/inoche

Synthesis of novel gold(I) complexes derived by AgCl-elimination between [AuCl(PPh_3)] and silver(I) heterocyclic carboxylates, and their antimicrobial activities. Molecular structure of [Au(*R,S*-Hpyrrld)(PPh_3)] (H_2pyrrld = 2-pyrrolidone-5-carboxylic acid)

Ryusuke Noguchi, Akihiro Hara, Akiyoshi Sugie, Kenji Nomiya *

Department of Materials Science, Faculty of Science, Kanagawa University, Tsuchiya, Hiratsuka, Kanagawa 259-1293, Japan

Received 17 December 2005; accepted 12 January 2006
Available online 2 March 2006

Abstract

Novel gold(I) complexes with hard (O donor) and soft (P donor) Lewis bases, [Au(*R*,*S*-Hpyrrld)(PPh_3)] · $CHCl_3$ **1** (H_2pyrrld = 2-pyrrolidone-5-carboxylic acid) and [Au(*R*,*S*-othf)(PPh_3)] **2** (Hothf = 5-oxo-2-tetrahydrofurancarboxylic acid), were prepared by the AgCl elimination reaction in $CHCl_3$ between [AuCl(PPh_3)] and the Ag–O bonding precursors such as [Ag_2(*R*-Hpyrrld)(*S*-Hpyrrld)] and [Ag_2(*R*-othf)(*S*-othf)]. Molecular structure of **1** was determined as a discrete monomer of the 2-coordinate AuOP core. In the preparation of **1** and **2**, the use of the Ag–O bonding precursors is crucial. Both complexes **1** and **2** showed selective antimicrobial activities against Gram-positive bacteria and yeasts.

Keywords: Gold(I) complexes; Triphenylphosphine; 2-Pyrrolidone-5-carboxylic acid; 5-Oxo-2-tetrahydrofurancarboxylic acid; X-ray crystal structure; Antimicrobial activities

There is considerable interest in the coordination chemistry of coinage metal (silver(I) and gold(I)) complexes with biological and pharmacological activity. In bioinorganic chemistry of coinage metal(I) complexes, there have been reported various studies of gold(I) complexes related to their antiarthritic [1–3], antitumor [2–6], anti-HIV [2,3] and antimicrobial activities [7–12] and those of silver(I) complexes related to their antiethylene [13–15], antimicrobial [16–24], antitumor [25] and antiviral activities [26,27]. The molecular design of such silver(I) and gold(I) complexes is an intriguing aspect of the bioinorganic chemistry of metal-based drugs.

Recently, we have prepared several water-soluble, light-stable chiral silver(I) carboxylates {[Ag(Hpyrrld)]$_2$}$_n$ [16,17], {[Ag(othf)]$_2$}$_n$ [18], {[Ag(Hasp)]$_2$}$_n$ [19], {[Ag_2(ca)$_2$]}$_n$ and {[Ag_2(ca)$_2$(Hca)$_2$]}$_n$ [20] using chiral heterocyclic carboxylate ligands such as H_2pyrrld (H_2pyrrld = (*S*)-(−)- and (*R*)-(+)-2-pyrrolidone-5-carboxylic acid), Hothf (Hothf = (*S*)-(+)- and (*R*)-(−)-5-oxo-2-tetrahydrofurancarboxylic acid), H_2asp (H_2asp = D- and L-aspartic acid) and Hca (Hca = camphanic acid ($C_{10}H_{14}O_4$), i.e., (1*R*,4*S*)- and (1*S*, 4*R*)-4,7,7-trimethyl-3-oxo-2-oxabicyclo-[2.2.1]-heptane-1-carboxylic acid). These Ag–O bonding complexes have shown a wide spectrum of effective antimicrobial activities against bacteria, yeast and molds [16–20].

On the other hand, the antimicrobial test by 2-coordinate AuSP and AuNP complexes such as [Au(L)(PPh_3)] (HL = 2-mercaptopropionic acid (2-H_2mpa), 6-mercaptonicotinic acid (6-H_2mna), 2-mercaptonicotinic acid (2-H_2mna), D-penicillamine (D-H_2pen), D,L-penicillamine (D,L-H_2pen), 2-mercaptobenzoic acid (2-H_2mba), 3-mercaptobenzoic acid (3-H_2mba), 4-mercaptobenzoic acid (4-H_2mba), imidazole (Him), pyrazole (Hpz), 1,2,3-triazole (1,2,3-Htriz), 1,2,4-triazole (1,2,4-Htriz), tetrazole (Htetz)) has shown selective and effective activities against two

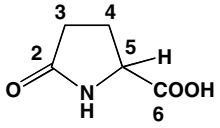
* Corresponding author. Tel.: +81 463 59 4111; fax: +91 463 58 9684.
E-mail address: nomiya@chem.kanagawa-u.ac.jp (K. Nomiya).

1387-7003/$ - see front matter © 2006 Elsevier B.V. All rights reserved.
doi:10.1016/j.inoche.2006.01.001

Gram-positive bacteria (*Bacillus subtilis*, *Staphylococcus aureus*) and modest activities against one or two yeasts (*Candidae albicans*) [11,12]. Thus, we have aimed at synthesizing novel PPh_3-gold(I) complexes with O-donor ligands such as $Hpyrrld^-$ and $othf^-$ in order to examine if the AuOP-core complexes show selective and effective activities against Gram-positive bacteria and yeasts. There have been reported only a few examples of the 2-coordinate AuOP complexes by Jones's group, e.g., $[Au(C_2H_3O_2)(PPh_3)]$ ($C_2H_3O_2$ = acetate) [28], $[Au(C_7H_5O_2)(PPh_3)]$ ($C_7H_5O_2$ = benzoate) [29], $[Au(O_2C\text{-}CH_2NHC(O)Ph)(PPh_3)]$ ($O_2CCH_2NHC(O)Ph$ = hippurate) [30].

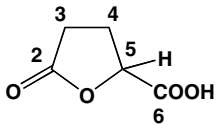
In this work, we have examined the AgCl elimination reaction in $CHCl_3$ between $[AuCl(PPh_3)]$ [31] and the Ag–O bonding precursor ($[Ag(Hpyrrld)]_2$ [16,17] or $[Ag(othf)]_2$ [18]) and obtained two light-stable, novel gold(I) complexes with hard (O donor) and soft (P donor) Lewis bases, i.e., $[Au(R,S\text{-Hpyrrld})(PPh_3)]\cdot CHCl_3$ **1** [32] and $[Au(R,S\text{-othf})(PPh_3)]$ **2** [33]. These complexes were characterized with elemental analysis, TG/DTA, FTIR, solution (^1H, ^{13}C, ^{31}P) NMR and X-ray crystallography. Their antimicrobial activities against selected bacteria, yeast and molds were also tested.

Herein we report the synthesis and characterization of **1** and **2**, including the crystal and molecular structures of **1**, and their antimicrobial activities.



2-pyrrolidone-5-carboxylic acid

(H_2pyrrld)



5-oxo-2-tetrahydrofurancarboxylic acid

(Hothf)

The molecular formulas of **1** and **2** were consistent with all data of elemental analysis, TG/DTA, FTIR, solution (^1H, ^{13}C, ^{31}P) NMR spectra and, also, X-ray structure analysis. Complex **1** was synthesized by reaction of the dimeric silver(I) carboxylate precursor $[Ag(Hpyrrld)]_2$ with the gold(I) precursor $[AuCl(PPh_3)]$ in $CHCl_3$ [32]. Colorless crystals of **1** soluble in most organic solvents were obtained in 67.9% (0.24 g) yield by a vapor diffusion with $CHCl_3$/light petroleum system as the internal/external solvents. Complex **2** as a colorless crystalline compound soluble in most organic solvents was obtained in 59.5% (0.35 g) yield by reaction of $[Ag(othf)]_2$ with $[AuCl(PPh_3)]$ in $CHCl_3$ [33].

Synthetic reactions of **1** and **2**, both based on AgCl elimination between the two precursors, are shown as follows:

$$[Ag_2(R\text{-Hpyrrld})(S\text{-Hpyrrld})] + 2[AuCl(PPh_3)] \rightarrow 2[Au(R,S\text{-Hpyrrld})(PPh_3)]\mathbf{1} + 2AgCl$$

$$[Ag_2(R\text{-othf})(S\text{-othf})] + 2[AuCl(PPh_3)] \rightarrow 2[Au(R,S\text{-othf})(PPh_3)]\mathbf{2} + 2AgCl$$

In the preparation of **1** and **2**, the use of the Ag–O bonding precursor $[Ag(Hpyrrld)]_2$ or $[Ag(othf)]_2$ is crucial. For instance, the reactions among $[AuCl(PPh_3)]$, NaOH and HL (HL = *R*,*S*-H_2pyrrld, *R*,*S*-Hothf) did not give the target compounds **1** and **2**.

The presence of one solvated $CHCl_3$ molecule in **1** was confirmed by elemental analysis, weight loss observed in TG/DTA measurement and, also, X-ray crystallography. Complex **2** was obtained without any solvent molecules. FTIR spectra of **1** and **2** confirmed the presence of coordinated PPh_3 molecules as typical, intense vibrational bands.

The ^{31}P NMR spectra in $CDCl_3$ of **1** and **2** showed only one resonance at around δ 28.0, the chemical shift of which can be compared with the signal at δ 29.4 of the related AuOP complex, $[Au(O_2CNEt_2)(PPh_3)]$ ($O_2CNEt_2^-$ = *N*,*N*′-diethylcarbamato) [34].

The ^1H NMR spectra in $CDCl_3$ of **1** and **2** showed signals of the coordinating heterocyclic ligands consisting of multiplet peaks for the two methylene groups (H4 and H3) and double doublet peaks (four lines) for the H5 proton within the ring, as well as a single peak for NH proton for **1**, in addition to signals of the coordinating PPh_3 ligand. The ^{13}C NMR spectra in $CDCl_3$ of **1** and **2** showed the (C4, C3, C5, C6 and C2) signals for the coordinating $Hpyrrld^-$ and $othf^-$ ligands, respectively.

X-ray structure analysis of **1** revealed the almost linear 2-coordinate gold(I) complex with AuOP core with $Hpyrrld^-$ and PPh_3 ligands (Au1–O3 2.072(3), Au1–P1 2.2137(16) Å, O3-Au1-P1 176.61(10)°) (Fig. 1) [35]. Complex **1** was a discrete monomer without any intermolecular interaction. The coordinating oxygen atom was based on the carboxyl oxygen, but not the carbonyl oxygen. The solvated $CHCl_3$ molecule was found in the crystal structure, although it was highly disordered. In the unit cell, a combination of two *R*-forms and two *S*-forms ($Z = 4$), i.e., a racemic mixture, was found.

The bond distances and angles of the AuOP core in **1** can be compared with those of a couple of examples of neutral 2-coordinate O–Au(I)–P complexes such as

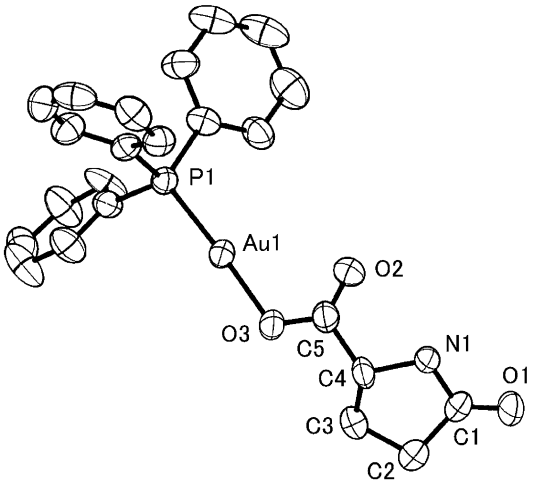


Fig. 1. Molecular structure of $[Au(R,S\text{-Hpyrrld})(PPh_3)]\cdot CHCl_3$ **1** with 50% probability ellipsoids. Selected interatomic distances (Å) and angles (°): Ag1-O3 2.072(3), Au-P1 2.2137(16) Å; O3-Au1-P1 176.61(10)°.

$[Au(C_2H_3O_2)(PPh_3)]$ (Au–O 2.063(6), Au–P 2.207(3) Å, O–Au–P 177.3(2)°) [28], $[Au(C_7H_5O_2)(PPh_3)]$ (Au–O 2.033(6), Au–P 2.213(3) Å, O–Au–P 173.7(2)°) [29], $[Au(O_2CCH_2NHC(O)Ph)(PPh_3)]$ (Au–O 2.077(5), Au–P 2.212(2) Å, O–Au–P 174.6(1)°) [30].

Antimicrobial activities, estimated by minimum inhibitory concentration (MIC; $\mu g\,ml^{-1}$), of the 2-coordinate gold(I)–PPh_3 complexes with AuOP cores **1** and **2** are shown in Table 1, together with the prototypical results of the previously reported complexes [Au(D-Hpen)(PPh_3)], [Au(D,L-Hpen)(PPh_3)] · 0.5MeOH and [Au(4-Hmba)(PPh_3)] · 0.3(acetone) with AuSP core [12] and [Au(1,2,3-triz)(PPh_3)] with AuNP core [11], and free *R*,*S*-H_2pyrrld and *S*-Hothf ligands. All of these complexes were water insoluble, and the antimicrobial test was carried out in a suspension of aqueous media.

As for several phosphinegold(I) complexes with N–Au–P and S–Au–P cores, regardless of whether in a homogeneous organic system or a heterogeneous aqueous suspension, the common activities have been observed, i.e., selective antimicrobial activities against two Gram-positive bacteria (*B. subtilis, S. aureus*) and modest activities against one or two yeasts (*C. albicans*) [11,12], which were well correlated with their ligand-exchangeability, i.e. with the identity of the complex.

Complex **2** showed selective and effective activities against two Gram-positive bacteria (*B. subtilis*, *S. aureus*) and modest activities against two yeasts (*C. albicans*, *S. cerevisiae*), but it showed no activity against Gram-negative bacteria (*Escherichia coli, Pseudomonas aeruginosa*) and molds (*Aspergillus niger*, *P. citrinum*). Complex **1** showed modest activities against only one Gram-positive bacterium (*S. aureus*) and poor activities against two yeasts (*C. albicans*, *S. cerevisiae*). These antimicrobial activities and the spectra are essentially consistent with the previous results [11,12]. Thus, we can conclusively propose that the observed antimicrobial activities are commonly observed for the 2-coordinate gold(I)-PPh_3 complexes with AuOP, AuSP and AuNP cores. The subtly different activities between **1** and **2** may come from the presence of solvated $CHCl_3$ molecule in **1**. In fact, the separately prepared, fresh powder sample without any solvated molecules [Au(*R*,*S*-Hpyrrld)(PPh_3)] (**1a**) showed the effective activities against two Gram-negative bacteria (*E. coli*, *P. aeruginosa*) and modest activities against two yeasts (*C. albicans*, *S. cerevisiae*) as commonly observed in other phosphinegold(I) complexes without solvated molecules. Also, relating to these facts, the previously reported gold(I) complexes with solvated molecules, e.g., [Au(D,L-Hpen)(PPh_3)] · 0.5MeOH [12] and [Au(4-Hmba)(PPh_3)] · 0.3(acetone) [12], have shown modest activities against only one Gram-positive bacterium (*S. aureus*).[1]

Table 1
Antimicrobial activities of complexes **1**, **2**, related gold(I) complexes and "free ligands" evaluated by MIC ($\mu g\ mL^{-1}$)

	R,*S*-H_2pyrrld	*S*-Hothf	[Au(*R*,*S*-Hpyrrld)(PPh_3)] · $CHCl_3$ **1**	[Au(*R*,*S*-Hpyrrld)(PPh_3)] **1a**	[Au(*R*,*S*-othf)(PPh_3)] **2**	[Au(1,2,3-triz)(PPh_3)][a]	[Au(D-Hpen)(PPh_3)][b]	[Au(D,L-Hpen)(PPh_3)] · 0.5MeOH[b]	[Au(4-Hmba)(PPh_3)] · 0.3(acetone)[b,c]
Escherichia coli	>1000	>1000	>1000	>1000	>1000	>1000	>1000	>1000	>1000
Bacillus subtilis	>1000	>1000	>1000	62.5	31.3	7.9	125	>1000	>1000
Staphylococcus aureus	>1000	>1000	125	62.5	31.3	7.9	31.3	31.3	125
Pseudomonas aeruginosa	>1000	>1000	>1000	>1000	>1000	>1000	>1000	>1000	>1000
Candida albicans	>1000	>1000	500	500	125	250	250	>1000	>1000
Saccharomyces cerevisiae	>1000	>1000	500	500	125	500	250	>1000	>1000
Aspergillus niger	>1000	>1000	>1000	>1000	>1000	>1000	>1000	>1000	>1000
Penicillium citrinum	>1000	>1000	>1000	>1000	>1000	>1000	>1000	>1000	>1000

[a] Ref. [11].
[b] Ref. [12].
[c] See the footnote in the text.

[1] In Table 7 in Ref. [12] the antimicrobial activities by [Au(4-Hmba)(PPh_3)] · 0.3(acetone) have been erroneously described as MIC 125 for *B. subtilis*, which should be corrected as MIC 125 for *S. aureus*.

In summary, two novel gold(I) complexes with hard (O donor) and soft (P donor) Lewis bases, **1** and **2**, were synthesized from the water-soluble, light-stable silver(I)–oxygen bonding precursors and their selective antimicrobial activities against selected Gram-positive bacteria and yeasts were confirmed. The antimicrobial results were consistent with the previously reported results [11,12]. The crystal and molecular structures of **1** were successfully determined. The present gold(I) complexes are labile and will probably be precursors for other gold(I) complexes.

Acknowledgement

This work was supported by a High-tech Research Center Project from the Ministry of Education, Culture, Sports, Science and Technology, Japan.

Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.inoche.2006.01.001.

References

[1] M.C. Gimeno, A. Laguna, Comprehensive Coordination Chemistry II, vol. 6, Elsevier, Oxford, 2004, p. 911.
[2] C.F. Shaw III, Chem. Rev. 99 (1999) 2589.
[3] C.F. Shaw III, in: N.P. Farrell (Ed.), Uses of Inorganic Chemistry in Medicine, RSC, UK, 1999, p. 26 (Chapter 3).
[4] M.J. McKeage, P. Papathanasiou, G. Salem, A. Sjaarda, G.F. Swiegers, P. Waring, S.B. Wild, Metal-Based Drugs 5 (1998) 217.
[5] P.J. Barnard, M.V. Baker, S.J. Berners-Prince, D.A. Day, J. Inorg. Biochem. 98 (2004) 1642.
[6] L. Messori, G. Marcon, Met. Ions Biol. Syst. 42 (2004) 385.
[7] F. Novelli, M. Recine, F. Sparatore, C. Juliano, Il Farmaco 54 (1999) 232.
[8] S.P. Fricker, Gold Bull. 29 (1996) 53.
[9] A.M. Elsome, J.M.T. Hamilton-Miller, W. Brumfitt, W.C. Noble, J. Antimicrob. Chemother. 37 (1996) 911.
[10] S.J. Berners-Price, R.K. Johnson, A.J. Giovenella, L.F. Faucette, C.K. Mirabelli, P.J. Sadler, J. Inorg. Biochem. 33 (1988) 285.
[11] K. Nomiya, R. Noguchi, K. Ohsawa, K. Tsuda, M. Oda, J. Inorg. Biochem. 78 (2000) 363.
[12] K. Nomiya, S. Yamamoto, R. Noguchi, H. Yokoyama, N.C. Kasuga, K. Ohyama, C. Kato, J. Inorg. Biochem. 95 (2003) 208.
[13] H. Veen, A.A.M. Kwakkenbos, Sci. Hortic. (Amsterdam) 18 (1982,1983) 277.
[14] H. Veen, Sci. Hortic. (Amsterdam) 20 (1983) 211.
[15] K.M. Davies, G.E. Hobson, D. Grierson, Plant. Cell Environ. 11 (1988) 729.
[16] K. Nomiya, S. Takahashi, R. Noguchi, S. Nemoto, T. Takayama, M. Oda, Inorg. Chem. 39 (2000) 3301.
[17] K. Nomiya, S. Takahashi, R. Noguchi, J. Chem. Soc., Dalton Trans. (2000) 4369.
[18] K. Nomiya, S. Takahashi, R. Noguchi, J. Chem. Soc., Dalton Trans. (2000) 1343.
[19] K. Nomiya, H. Yokoyama, J. Chem. Soc., Dalton Trans. (2002) 2483.
[20] N.C. Kasuga, A. Sugie, K. Nomiya, J. Chem. Soc., Dalton Trans. (2004) 3732.
[21] S. Chen, G. Wu, H. Zeng, Carbohydr. Polym. 60 (2005) 33.
[22] N.V. Loginova, A.A. Chernyavskaya, G.I. Polozov, T.V. Koval'chuk, E.V. Bondarenke, N.P. Osipovich, A.A. Sheryakov, O.I. Shadyro, Polyhedron 24 (2005) 611.
[23] A. Melaiye, Z. Sun, K. Hindi, A. Milsted, D. Ely, D.H. Reneker, C.A. Tessier, W.J. Youngs, J. Am. Chem. Soc. 127 (2005) 2285.
[24] M.A.A. O'Neill, G.J. Vine, A.E. Beezer, A.H. Bishop, J. Hadgraft, C. Labetoulle, M. Chloe, P.G. Bowler, Int. J. Pharm. 270 (2004) 323.
[25] B. Coyle, M. McCann, K. Kavanagh, M. Devereux, V. Mckee, N. Nayal, D. Egan, C. Deegan, G.J. Finn, J. Inorg. Biochem. 98 (2004) 1361.
[26] P.C. Zachariadis, S.K. Hadjikakou, N. Hadjiliadis, S. Skoulika, A. Michaelides, J. Balzarini, E.D. Clercq, Eur. J. Inorg. Chem. 7 (2004) 1420.
[27] P.C. Zachariadis, S.K. Hadjikakou, N. Hadjiliadis, A. Michaelides, S. Skoulika, Y. Ming, Y. Xiaolin, Inorg. Chim. Acta 343 (2003) 361.
[28] P.G. Jones, Acta Crystallogr. C40 (1984) 1320.
[29] P.G. Jones, Acta Crystallogr. C41 (1985) 905.
[30] P.G. Jones, R. Schelbach, J. Chem. Soc., Chem. Commun. (1988) 1338.
[31] M.I. Bruce, B.K. Nicholson, O.B. Shawkataly, Inorg. Synth. 26 (1986) 324.
[32] [Au(*R*,*S*-Hpyrrld)(PPh_3)] · $CHCl_3$ **1**: To the solution of 0.247 g (0.50 mmol) of the gold(I) precursor [AuCl(PPh_3)] dissolved in 30 mL $CHCl_3$ was added 0.472 g (1.00 mmol) of the meso-form of silver(I) complex [Ag_2(*R*-Hpyrrld)(*S*-Hpyrrld)]. After stirring for one day, white–violet powder of AgCl produced was filtered off through a membrane filter (JV 0.1 μm). The colorless clear filtrate was evaporated to dryness with a rotary evaporator at 30 °C. The residue was dissolved in 10 mL $CHCl_3$, followed by filtering through a folded filter paper (Whatman #5). The clear filtrate was added dropwise to 200 mL light petroleum. A white precipitate was collected on a membrane filter (JV 0.1 μm), washed with light petroleum (50 mL × 2) and dried in vacuo for 2 h. The white powder was redissolved in 20 mL $CHCl_3$ and the solution was passed thorough a folded filter paper (Whatman #5). Vapor diffusion at 10 °C was performed using the filtrate as an inner solution and 100 mL light petroleum as an outer solvent. After ten days, colorless needle crystals deposited, which were collected on membrane filter (JV 0.1 μm), washed with light petroleum (50 mL × 2), thoroughly dried by suction and dried in vacuo for 2 h. Colorless needle crystals, obtained in 67.9% (0.24 g scale) yield, were soluble in most organic solvents and insoluble in water, light petroleum, Et_2O and hexane. Found: C, 40.84; H, 3.02; N, 1.98. Calc. for $C_{24}H_{22}NCl_3PO_3Au$ or [Au(Hpyrrld)(PPh_3)] · $CHCl_3$: C, 40.79; H, 3.14; N, 1.98%. TG/DTA data: weight loss of 14.5% was observed below 152 °C (calc. for 1.0 $CHCl_3$, 16.9%). Decomposition began around 136 °C with endothermic peaks at 112, 274 °C and exothermic peaks at 166, 345 °C. Prominent IR bands in the 1700–400 cm^{-1} region (KBr disk): 1676vs, 1589vs, 1478m (PPh_3), 1434s (PPh_3), 1408s, 1298s, 1179w, 1101s (PPh_3), 1026w, 998w, 747vs (PPh_3), 713s (PPh_3), 692vs (PPh_3), 545vs (PPh_3), 500vs (PPh_3) cm^{-1}. ^1H NMR ($CDCl_3$, 23.9 °C): δ 2.32–2.50 (4H, m, H3 and H4), 4.25 (1H, dd, H5), 5.95 (1H, s, NH), 7.48–7.56 (15H, m, Aryl). ^{13}C NMR ($CDCl_3$, 25.1 °C): δ 26.7 (C4), 27.5 (C3), 79.1 (C5), 128.1 (d, J_{CP} 65.5 Hz, Ph), 129.1 (d, J_{CP} 12.4 Hz, Ph), 131.9 (d, J_{CP} 2.5 Hz, Ph), 134.0 (d, J_{CP} 14.1 Hz, Ph), 174.4 (C6), 177.1 (C2). ^{31}P NMR ($CDCl_3$, 24.1 °C): δ 28.0. The separately prepared, chiral complexes [Au(*R*-Hpyrrld)(PPh_3)] and [Au(*S*-Hpyrrld)(PPh_3)], were difficult to crystallize by vapor diffusion of the inner $CHCl_3$ solution with the outer solvent hexane in a refrigerator at 4 °C, but they oiled. The powder sample without solvated $CHCl_3$ molecule **1a**, obtained before crystallization, was also used for the antimicrobial test.
[33] [Au(*R*,*S*-othf)(PPh_3)] **2**: Complex **2** was prepared by a 1:2 molar-ratio reaction in 60 mL of $CHCl_3$ of [Ag_2(*R*-othf)(*S*-othf)] (0.948 g, 2.00 mmol) with [AuCl(PPh_3)] (0.495 g, 1.00 mmol). By a similar work-up to synthesis of **1**, a colorless powder of **2** was obtained in 59.5% (0.35 g scale) yield, which was soluble in most organic solvents and insoluble in water, Et_2O, hexane and light petroleum. Found: C, 46.90; H, 3.29. Calc. for $C_{23}H_{20}O_4PAu$ or [Au(othf)(PPh_3)]: C, 46.95; H, 3.43%. TG/DTA data: no weight loss was observed before decomposition. Decomposition began around 166 °C with an endothermic peak at 184 °C and exothermic peaks at 200, 263 °C.

Prominent IR bands in the 1800–400 cm^{-1} region (KBr disk): 1780vs, 1652vs, 1624m, 1437s (PPh_3), 1379m, 1281m, 1253s, 1180m, 1154s, 1102s (PPh_3), 1056m, 1039m, 998m, 754s (PPh_3), 712s (PPh_3), 693vs (PPh_3), 545vs (PPh_3), 509vs (PPh_3) cm^{-1}. ^1H NMR ($CDCl_3$, 24.5 °C): δ 2.40–2.70 (4H, m, H3 and H4), 4.98 (1H, dd, H5), 7.48–7.56 (15H, m, Aryl). ^{13}C NMR ($CDCl_3$, 25.1 °C): δ 26.7 (C4), 27.5 (C3), 79.1 (C5), 128.1 (d, J_{CP} 65.5 Hz, Ph), 129.1 (d, J_{CP} 12.4 Hz, Ph), 131.9 (d, J_{CP} 2.5 Hz, Ph), 134.0 (d, J_{CP} 14.1 Hz, Ph), 174.4 (C6), 177.1 (C2). ^{31}P NMR ($CDCl_3$, 24.6 °C): δ 28.1. Complex **2** was crystallized by vapor diffusion of the inner $CHCl_3$ solution with the outer solvent hexane in a refrigerator at 4 °C, but the crystals were not suitable for X-ray diffraction measurements. The separately prepared, chiral complexes [Au(*R*-othf)(PPh_3)] and [Au(*S*-othf)(PPh_3)], were not crystallized, but oiled.

[34] R. Alessio, D.B. Dell'Amico, F. Calderazzo, U. Englert, A. Guarini, L. Labella, P. Strasser, Helv. Chim. Acta 81 (1998) 219.

[35] The intensity data were collected at 90 K on a Bruker SMART/APEX CCD diffractometer. The structure was solved by direct methods (SHELXTL version 5.10), and refined by a full-matrix least-squares on F^2. Crystal data for **1**: $C_{23}H_{21}AuNO_3P \cdot CHCl_3$; $M = 706.74$, monoclinic, space group $P2_1/n$, $a = 9.092(7)$, $b = 27.68(2)$, $c = 10.628(8)$ Å, $\beta = 107.818(12)°$, $V = 2546(3)$ $Å^3$, $Z = 4$, $D_c = 1.844$ g cm^{-3}, μ(Mo Kα) = 6.182 mm^{-1}. $R1 = 0.0519$, $wR2 = 0.1022$ (for all data). $R_{int} = 0.0545$, $R1 = 0.0392$, $wR2 = 0.0965$, GOF = 1.087 (6180 total reflections, 4909 unique reflections where $I > 2\sigma(I)$). The details of the crystal data have been deposited with Cambridge Crystallographic Data Centre as supplementary publication no. CCDC 259302 for **1**.