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Syntheses, Structures, and Antimicrobial Activities of Light-Stable and Di- and Mononuclear Silver(I) Carboxylate Complexes Composed of Triphenylphosphine, and Chiral and Racemic Forms of 2-Pyrrolidone-5-carboxylic Acid (H_2pyrrld). A Variety of Ag–O Bonding Modes in the Silver(I) Complexes Constructed with Hard Oxygen and Soft Phosphorus Atoms

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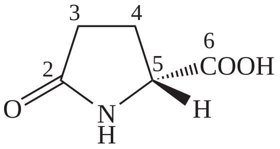
Using light-stable dimeric silver(I) carboxylate precursors $\{[Ag(Hpyrrld)]_2\}_n$ formed with chiral and racemic forms of 2-pyrrolidone-5-carboxylic acid (H_2pyrrld) ligand, six novel light-stable, triphenylphosphinesilver(I) complexes consisting of both a hard Lewis base (O atom) and a soft Lewis base (P atom) were prepared, i.e. $[Ag_2(R\text{-}Hpyrrld)_2(H_2O)(PPh_3)_2]\cdot H_2O$ (**1**), $[Ag(R\text{-}Hpyrrld)(PPh_3)_2]_2$ (**2**), $[Ag_2(S\text{-}Hpyrrld)_2(H_2O)(PPh_3)_2]\cdot H_2O$ (**3**), $[Ag(S\text{-}Hpyrrld)(PPh_3)_2]_2$ (**4**), $\{[Ag(R,S\text{-}Hpyrrld)(PPh_3)]_2\}_n$ (**5**), and $[Ag(R,S\text{-}Hpyrrld)(PPh_3)_2]$ (**6**). Their solid-state and solution structures were unequivocally characterized with elemental analysis, TG/DTA, FTIR, X-ray structure analysis, molecular weight measurements in EtOH with the vaporimetric method, solution (^1H, ^{13}C, and ^{31}P) NMR, and solid-state ^{31}P CPMAS NMR spectroscopy. Two sets of the enantiomeric complexes were isolated as (**1** and **3**) and (**2** and **4**). X-ray crystallography revealed that these complexes possessed different Ag–O bonding modes, depending on the number of PPh_3 ligands and the chirality of the $Hpyrrld^-$ ligand. The complexes **1**–**6** behaved as a monomeric species in EtOH and CD_2Cl_2. The antimicrobial activites by the silver(I) complexes in the water–suspension system against selected bacteria, yeast, and molds, were significantly correlated with the number of coordinating PPh_3 ligands per silver(I) atom in the complexes.

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 only a few biological and medicinal studies of silver(I) complexes, in comparison with many studies of gold(I) complexes related to their antiarthritic,[1] antitumor,[1b,c,2] anti-HIV,[1b,c] and also, recently, antimicrobial activities.[3] The studies of silver(I) complexes have been mostly related to their antiethylene[4] and antimicrobial activities.[5,6] The molecular design of such silver(I) and gold(I) complexes are an intriguing aspect of the bioinorganic chemistry of metal-based drugs.

In the past decade, the antimicrobial activities of Ag(I) and Au(I) complexes have been actively studied.[3,5,6] The antimicrobial activities by metal complexes primarily depend on the metal ions and, therefore, the different metal centers in the complexes brought about the different activities. The intrinsic ease of ligand replacement of the Ag–O bonding complexes due to low affinity between a hard Lewis base (oxygen atom) and a soft Lewis acid (silver(I) atom) would permit a direct interaction of such complexes with biological ligands, resulting in the formation of silver(I)–biological ligand complexes, i.e. growth inhibition of microorganisms. Thus, the antimicrobial activities by coinage metal complexes depend on whether or not the complexes can possess further ligand-replacement ability with the biological ligands.[6] It has been also suggested[6] that one of the key factors determining the antimicrobial effects of silver(I) complexes is the nature of the atom coordinating to the silver(I) center and its bonding properties, rather than the solubility, charge, chirality, or degree of polymerization of the complexes.

In relation to this concept, Ag–O bonding complexes, e.g. silver(I) carboxylates, have attracted much attention as potential functional materials showing a wide spectrum of effective antimicrobial activities. However, silver(I) carboxylates are, in general, light-sensitive which, together with their poor solubility, makes structural characterization difficult.[1a] Recently, we have prepared several water-soluble, light-stable chiral silver(I) carboxylates using chiral heterocyclic carboxylate ligands: $\{[Ag(Hpyrrld)]_2\}_n$ (H_2pyrrld = (*S*)-(−)- and (*R*)-(+)-2-pyrrolidone-5-carboxylic acid) (Chart 1),[6a,b] $\{[Ag(othf)]_2\}_n$ (Hothf = (*S*)-(+)- and (*R*)-(−)-5-oxo-2-tetrahydrofurancar-



R-H_2pyrrld

Chart 1.

boxylic acid),[6c] $\{[Ag(Hasp)]_2\}_n$ (H_2asp = D- and L-aspartic acid),[6d] $\{[Ag_2(ca)_2]\}_n$ (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), and $\{[Ag_2(ca)_2(Hca)_2]\}_n$.[6e] These complexes have shown a wide spectrum of effective antimicrobial activities against bacteria, yeast, and molds. Very recently, we have obtained the novel tetranuclear silver(I) cluster $[Ag(2\text{-Hmba})(PPh_3)]_4$ with a three-leaves propeller (C_3 symmetry) in the 1:2:2 moler-ratio reaction of $[Ag_2(R\text{-Hpyrrld})(S\text{-Hpyrrld})]$, PPh_3, and 2-H_2mba in a 1:4 mixed $CHCl_3$/EtOH solvent.[6f]

When a neutral donor ligand is incorporated in the silver carboxylate coordination sphere, other structures can be anticipated as, for example, with phosphine or ammine ligands.[1a] However, X-ray structure determination of silver(I) complexes with both hard (anionic *O*-donor ligand) and soft Lewis bases (e.g., PPh_3 ligand) have been scarcely reported so far. Thus, we have aimed at synthesizing the Ag(I)–O complexes with different Ag–O bonding modes by incorporating the triphenylphosphine ligand.

In this work, we have carried out the molar-ratio varied reactions of PPh_3 and the three well-characterized Ag–O bonding precursors, $\{[Ag(R\text{-Hpyrrld})]_2\}_n$, $\{[Ag(S\text{-Hpyrrld})]_2\}_n$, and $\{[Ag_2(R\text{-Hpyrrld})(S\text{-Hpyrrld})]\}_n$, in 1:4 solvent mixture of CH_2Cl_2 and EtOH. We have obtained six novel light-stable, silver(I) complexes, i.e. $[Ag_2(R\text{-Hpyrrld})_2(H_2O)(PPh_3)_2]\cdot H_2O$ (**1**), $[Ag(R\text{-Hpyrrld})(PPh_3)_2]_2$ (**2**), $[Ag_2(S\text{-Hpyrrld})_2(H_2O)(PPh_3)_2]\cdot H_2O$ (**3**), $[Ag(S\text{-Hpyrrld})(PPh_3)_2]_2$ (**4**), $\{[Ag(R,S\text{-Hpyrrld})(PPh_3)]_2\}_n$ (**5**), and $[Ag(R,S\text{-Hpyrrld})(PPh_3)_2]$ (**6**), characterized them with elemental analysis, thermogravimetric/differential thermal analysis (TG/DTA), FTIR, solution (^1H, ^{13}C, and ^{31}P) and solid-state ^{31}P CPMAS NMR, molecular weight measurements in EtOH, X-ray crystallography, and also tested their antimicrobial activites against selected bacteria, yeast, and molds in a water–suspension system. Complexes (**1** and **3**) and (**2** and **4**) are a set of enantiomers. X-ray crystallography revealed that the Ag–O bonding modes in **1**–**6** were quite different and strongly depended upon both chirality of the $Hpyrrld^-$ ligand and the number of the coordinating PPh_3 ligands. The complexes **1**–**6** and the dimeric silver(I) precursors were classified into four groups (Type I–IV) based on the Ag–O bonding modes. In terms of reactivity of these complexes, it was found the reaction from **1** and **3** formed the dimeric *meso*-form **5**, and that from **2** and **4** produced **6** as a racemic compound. The behavior as a monomeric species in EtOH and CD_2Cl_2 of **1**–**6** was also discussed based on molecular weight measurements in EtOH, ^{31}P NMR in CD_2Cl_2, and solid-state ^{31}P NMR spectroscopy. Significant correlation between the antimicrobial activity and the number of coordinating PPh_3 ligands per silver(I) atom was found.

Herein, we report full details of the synthesis of complexes **1**–**6**, their solution and solid-state characterization, the crystal and molecular structures, classification (Type I–IV) of the complexes based on the Ag–O bonding modes and their antimicrobial activities.

Experimental

Materials. The following were reagent grade and used as received: PPh_3, EtOH, CH_2Cl_2, $CHCl_3$, Et_2O, acetone, and light petroleum (bp: 30–60 °C) (all from Wako); CD_2Cl_2 (Isotec). The silver(I) precursors, $[Ag(R\text{-Hpyrrld})]_2$, $[Ag(S\text{-Hpyrrld})]_2$, and $[Ag_2(R\text{-Hpyrrld})(S\text{-Hpyrrld})]$, were prepared and identified according to the literature.[6a,b]

Instrumentation/Analytical Procedures. The CHN analyses were performed using Perkin-Elmer PE2400 series II CHNS/O Analyzer (Kanagawa University). Infrared spectra were recorded on a Jasco 4100 FT-IR spectrometer in KBr disks at room temperature. Thermogravimetric (TG) and differential thermal analyses (DTA) were acquired using a Rigaku TG8120 and Thermo Plus 2 system. TG/DTA measurements were run under air with a temperature ramp of 4 °C per min between 20 and 500 °C.

^1H (399.65 MHz), $^{13}C\{^1H\}$ (100.40 MHz), and $^{31}P\{^1H\}$ NMR (161.70 MHz) spectra in solution were recorded in 5-mm outer diameter tubes on a JEOL JNM-EX 400 FT-NMR spectrometer with a JEOL EX-400 NMR data processing system. ^1H and $^{13}C\{^1H\}$ NMR spectra of the complexes were measured in CD_2Cl_2 solution with reference to an internal TMS. Chemical shifts are reported as positive for resonances downfield of TMS ($\delta\,0$). ^{31}P NMR spectra were referenced to an external standard of 85% H_3PO_4 by a substitution method. Chemical shifts were reported on the δ scale with resonances upfield of H_3PO_4 ($\delta\,0$) as negative. Solid-state ^{31}P NMR (121.00 MHz) spectra were measured using a JEOL JNM-ECP 300 FT-NMR spectrometer equipped with a cross-polarization (CP)/magic angle spinning (MAS) accessory. The ^{31}P CPMAS NMR spectra were referenced to an external standard of $(NH_4)_2HPO_4$ by a substitution method at 23.0 °C and their chemical shifts were calibrated indirectly through an external $(NH_4)_2HPO_4$ ($\delta\,0$).

Molecular weight measurements in EtOH of complexes **1** and **2** with the vapor pressure osmometer were carried out by Mikroanalytishes Labor Pascher (Remagen, Germany) and evaluated for 15.69 mg of **1** dissolved in 0.3752 g of EtOH and 14.59 mg of complex **2** dissolved in 0.3962 g of EtOH.

Antimicrobial Activitiy. Antimicrobial activities of silver(I) complexes **1**, **2**, **5**, and **6** were estimated by the minimum inhibitory concentration (MIC: $\mu g\,mL^{-1}$) as shown elsewhere.[6] The antimicrobial tests of the water-soluble precursor $[Ag(R\text{-Hpyrrld})]_2$ and "free ligand" *R*-H_2pyrrld were carried out in a homogeneous aqueous media,[6b] while those of the organic-solvent soluble complexes, **1**, **2**, **5**, and **6** prepared here, were carried out in a water–suspension system.

$[Ag_2(R\text{-Hpyrrld})_2(H_2O)(PPh_3)_2]\cdot H_2O$ (1). To a suspension of 0.354 g (0.75 mmol) of $[Ag(R\text{-Hpyrrld})]_2$ dispersed in 10 mL of 1:4 (v/v) solvent mixture of CH_2Cl_2 and EtOH was added 0.262 g (1.00 mmol) of PPh_3. After stirring for 10 min, the white suspension was filtered off through a folded filter paper (Whatman #5). By adding slowly 120 mL of light petroleum to the colorless clear filtrate, two layers were formed. After a few days, colorless plate crystals deposited, which were collected on a membrane filter (JG 0.2 μm), thoroughly dried by suction and dried in vacuo for 2 h. Colorless plate crystals, obtained in 29.2% (0.151 g scale) yield, were soluble in most organic solvents and insoluble in water and light petroleum. Compound **1** was relatively unstable in solution: on standing the CH_2Cl_2 solution of **1** for a few days at room temperature, it decomposed to give a solid of the original precursor $[Ag(R\text{-Hpyrrld})]_2$, and compound **2** was formed in solution.

$[Ag(R\text{-Hpyrrld})(PPh_3)_2]_2$ (2). Compound **2** was prepared by a 1:4 molar-ratio reaction in 10 mL of a solvent mixture (CH_2Cl_2:EtOH = 1:4 (v/v)) of $[Ag(R\text{-Hpyrrld})]_2$ (0.236 g, 0.50 mmol) and PPh_3 (0.525 g, 2.0 mmol). By the similar work-up described above, colorless plate crystals of **2** were obtained in 53.0%

(0.403 g scale) yield, which were soluble in most organic solvents and insoluble in water and light petroleum.

$[Ag_2(S\text{-Hpyrrld})_2(H_2O)(PPh_3)_2]\cdot H_2O$ (3). The precursor $[Ag(S\text{-Hpyrrld})]_2$ was used instead of $[Ag(R\text{-Hpyrrld})]_2$ in the synthesis of **1**. Colorless plate crystals of **3**, soluble in most organic solvents and insoluble in water and light petroleum, were obtained in 30.4% (0.157 g scale) yield.

$[Ag(S\text{-Hpyrrld})(PPh_3)_2]_2$ (4). The precursor $[Ag(S\text{-Hpyrrld})]_2$ was used in the place of $[Ag(R\text{-Hpyrrld})]_2$ in the synthesis of **2**. Colorless plate crystals of **4**, soluble in most organic solvents and insoluble in water and light petroleum, were obtained in 69.9% (0.532 g scale) yield.

$\{[Ag(R,S\text{-Hpyrrld})(PPh_3)]_2\}_n$ (5). In the preparation of **1**, the *meso*-form precursor $[Ag_2(R\text{-Hpyrrld})(S\text{-Hpyrrld})]$ (0.354 g, 0.75 mmol) dissolved in 15 mL of 1:4 (v/v) solvent mixture of CH_2Cl_2 and EtOH, and 0.262 g (1.00 mmol) of PPh_3 were used. Colorless clear cubic crystals of **5** were obtained in 25.9% (0.129 g scale) yield, which were soluble in DMSO, $CHCl_3$, and CH_2Cl_2, sparingly soluble in EtOH, and insoluble in acetone, water, light petroleum, and Et_2O.

Reaction from Complexes 1 and 3 Producing Complex 5.

$$[Ag_2(R\text{-Hpyrrld})_2(H_2O)(PPh_3)_2]\ (\mathbf{1}) + [Ag_2(S\text{-Hpyrrld})_2(H_2O)(PPh_3)_2]\ (\mathbf{3}) \rightarrow 2/n\{[Ag(R,S\text{-Hpyrrld})(PPh_3)]_2\}_n\ (\mathbf{5}). \quad (1)$$

To a suspension of $[Ag(R\text{-Hpyrrld})]_2$ (0.236 g, 0.50 mmol) in 15 mL of a solvent mixture of CH_2Cl_2 and EtOH (1:4 (v/v)) was added 0.262 g (1.00 mmol) of PPh_3, followed by stirring for 30 min. In the solution, $[Ag_2(R\text{-Hpyrrld})_2(H_2O)(PPh_3)_2]$ (**1**) is formed. The 1:1 mixture of the in situ-generated complex **1** and its enantiomer **3** in solution was prepared: to the clear colorless filtrate of **1** obtained by passing through a folded filter paper (Whatman #5) was added the filtrate of the enantiomer **3**. After stirring the mixture for 1 h, the solution was passed through a folded filter paper (Whatman #5). Along an interior wall of the beaker containing the clear colorless filtrate was slowly spread 85 mL of light petroleum. The beaker containing the two phases composed of the filtrate in the lower layer and the light petroleum in the upper layer was sealed and placed in the dark. After one day, clear colorless cubic crystals deposited, which were collected on a membrane filter (JG 0.2 μm) and dried in vacuo for 2 h. Colorless cubic crystals, obtained in 42.0% (0.418 g scale) yield, were soluble in DMSO, CH_2Cl_2, and $CHCl_3$, and insoluble in water, light petroleum, acetone, MeOH, EtOH, EtOAc, acetonitrile, and Et_2O. The product was characterized and identified with CHN analysis, TG/DTA, FTIR, solution (^1H, ^{13}C, and ^{31}P) NMR, and X-ray crystallography. The main product was complex **5**, but it was contaminated with a small amount of complex **6** with two PPh_3 ligands.

$[Ag(R,S\text{-Hpyrrld})(PPh_3)_2]$ (6). In the place of the precursors in the preparations of **2** and **4**, the *meso*-form precursor $[Ag_2(R\text{-Hpyrrld})(S\text{-Hpyrrld})]$ (0.236 g, 0.50 mmol) dissolved in 15 mL of 1:4 (v/v) solvent mixture of CH_2Cl_2 and EtOH, and 0.525 g (2.00 mmol) of PPh_3 were used. Colorless cubic crystals of **6**, obtained in 53.8% (0.409 g scale) yield, were soluble in DMSO, $CHCl_3$, and CH_2Cl_2, sparingly soluble in EtOH, and insoluble in acetone, water, light petroleum, and Et_2O.

Reaction from Complexes 2 and 4 Producing Complex 6.

$$[Ag(R\text{-Hpyrrld})(PPh_3)_2]_2\ (\mathbf{2}) + [Ag(S\text{-Hpyrrld})(PPh_3)_2]_2\ (\mathbf{4}) \rightarrow 4[Ag(R,S\text{-Hpyrrld})(PPh_3)_2]\ (\mathbf{6}). \quad (2)$$

Similar work-up in the reaction from complexes **1** and **3** producing complex **5**, except the use of 0.525 g (2.00 mmol) of PPh_3, was performed. Colorless cubic crystals, obtained in 44.0% (0.670 g scale) yield, were soluble in DMSO, CH_2Cl_2, and $CHCl_3$, sparingly soluble in EtOH, and insoluble in water, light petroleum, acetone, MeOH, EtOAc, acetonitrile, and Et_2O. This complex in solution was stable thermally and for light. The reaction product was a racemic compound **6** of the monomeric, 4-coordinate *R*- and *S*-complexes, which was identified with CHN analysis, TG/DTA, FTIR, solution (^1H, ^{13}C, and ^{31}P) NMR, and X-ray crystallography.

X-ray Cystallography. Liquid–liquid diffusion consisting of $CH_2Cl_2/EtOH$ mixed solvent in the lower layer and light petroleum in the upper layer gave colorless plate crystals for **1–4** and colorless cubic crystals for **5** and **6**. Crystals of sufficient quality suitable for single-crystal X-ray diffraction studies were grown.

Each single-crystal of silver(I) complexes **1–6** was mounted on “a loop” and used for measurements at 90 K of precise cell constants, intensity data were collected on a Bruker Smart CCD diffractometer (Mo Kα radiation, $\lambda = 0.71073$ Å). All calculations for the subsequent structure determination were carried out using the SHELXL (version 5.1).[7] All non-hydrogen atoms were refined anisotropically and hydrogen atoms isotropically. Crystal data, data collection, and structure refinement of **1–6** are summarized in Table 1.

Crystallographic data have been deposited at the CCDC, 12, Union Road, Cambridge, CB2 1EZ, UK (Fax: +44 1223 336033; e-mail: deposit@ccdc.cam.ac.uk) and copies can be obtained on request, free of charge via http://www.ccdc.cam.ac.uk/conts/retrieving.html, by quoting the publication citation and the deposition numbers CCDC 259296-259301.

Results and Discussion

Compositional Characterization. The molecular formulas of silver(I) complexes **1–6** prepared here were consistent with all data of elemental analysis, TG/DTA, FTIR, solid-state ^{31}P CPMAS NMR, solution (^1H, ^{13}C, and ^{31}P) NMR spectra, all as listed in Table 2 and, also, X-ray structure analysis. Silver(I) complexes of **2**, **4**, **5**, and **6** were isolated without any solvent molecules. The presence of one solvated water molecule and one water molecule bridged between two silver(I) atoms in **1** and **3** was confirmed by elemental analysis, weight loss observed in TG/DTA measurement, and X-ray crystallography. The solid-state FT-IR spectra of **1–6** showed the multiple vibrational bands based on the coordinating PPh_3 ligands. Upon complexation, the carbonyl stretching bands of the “free” ligand at 1720 and 1648 cm^{-1} were shifted, which were observed at 1656 and 1604 cm^{-1} for **1** and **3**, at 1679 and 1590 cm^{-1} for **2** and **4**, at 1665 and 1579 cm^{-1} for **5**, and at 1698 and 1589 cm^{-1} for **6**.

X-ray crystallography showed that **2** and **4** were discrete dimers, **1**, **3**, and **5** took supramolecular arrangements of the dimeric units, and **6** was a racemic compound of two extremely distorted 4-coordination monomers.

Crystal and Molecular Structures. The molecular structures of **1**, **2**, **5**, and **6** with the atom numbering scheme are depicted in Figs. 1–4, respectively. Selected bond distances and angles with their estimated standard deviations are listed in Table 3.

The molecular structure (Fig. 1a) of the dinuclear complex **1** was composed of two silver(I) centers, two monoanionic

Table 1. Crystallographic Data for Silver(I) Complexes **1**–**6**

Compound	**1**	**2**	**3**	**4**	**5**	**6**
Formula	$C_{46}H_{44}Ag_2N_2O_7P_2 \cdot H_2O$	$C_{82}H_{72}Ag_2N_2O_6P_4$	$C_{46}H_{44}Ag_2N_2O_7P_2 \cdot H_2O$	$C_{82}H_{72}Ag_2N_2O_6P_4$	$C_{46}H_{42}Ag_2N_2O_6P_2$	$C_{41}H_{36}AgNO_3P_2$
FW	1032.54	1521.12	1032.54	1521.12	996.53	760.52
T/K	90	90	90	90	90	90
Crystal color, shape	colorless, plate	colorless, plate	colorless, plate	colorless, plate	colorless, cubic	colorless, cubic
Crystal dimension/mm^3	0.28 × 0.26 × 0.02	0.54 × 0.38 × 0.28	0.25 × 0.17 × 0.04	0.14 × 0.12 × 0.07	0.21 × 0.17 × 0.08	0.33 × 0.28 × 0.10
Crystal system	Trigonal	Monoclinic	Trigonal	Monoclinic	Triclinic	Triclinic
Space group	$P3_221$	$P2_1$	$P3_121$	$P2_1$	$P\bar{1}$	$P1$
a/Å	9.4498(6)	10.6177(7)	9.507(7)	10.633(6)	8.6303(7)	12.8408(11)
b/Å	9.4498(6)	18.0392(11)	9.507(7)	18.079(9)	8.8133(7)	13.1955(11)
c/Å	43.158(5)	18.3897(11)	43.37(5)	18.444(10)	15.2483(13)	13.2511(11)
α/deg	90	90	90	90	88.8380(10)	112.2700(10)
β/deg	90	105.6050(10)	90	105.738(10)	74.7980(10)	97.417(2)
γ/deg	120	90	120	90	65.9770(10)	115.5170(10)
V/Å^3	3337.6(5)	3392.4(4)	3395(5)	3413(3)	1017.35(14)	1756.5(3)
D_x/Mg m^{-3}	1.568	1.489	1.542	1.480	1.627	1.440
μ(Mo Kα)/mm^{-1}	1.009	0.730	0.992	0.726	1.094	0.706
Z	3	1	3	1	1	2
Refln/param ratio	5531/288	16550/865	5467/288	16474/865	5048/262	15781/865
$R1$ [$I > 2\sigma(I)$]	0.0458	0.0245	0.0517	0.0437	0.0313	0.0311
$wR2$ (all refln)	0.0918	0.0651	0.1227	0.0802	0.0851	0.0869
GOF	1.243	1.023	1.299	0.874	1.027	0.692

Hpyrrld$^-$ ligands, two PPh_3 ligands, and one bridging water molecule. In the crystal structure, one water molecule of crystallization, which does not participate in the coordination, was also found. A weak interaction between two silver(I) atoms in **1** was found (Ag–Ag distance 3.2854(7) Å). The monodentate PPh_3 ligand was coordinated to the silver(I) center to form a bended line of P1–Ag1···Ag1^i–P1^i (Ag1–P1 distance 2.3312(10) Å, P1–Ag1–Ag1^i angle 163.68(3)°, P1–Ag1···Ag1^i–P1^i dihedral angle 46.84(11)°). One (O3, O3^i) of the oxygen atoms in the carboxyl group in the Hpyrrld$^-$ ligand was bridged unsymmetrically between the two silver(I) centers (Ag1–O3 distance 2.465(3) Å and Ag1–O3^i distance 2.341(3) Å). In the opposite site, the oxygen atom (O11) of the water molecule was bridged symmetrically between the two silver(I) centers (Ag1–O11 distance 2.438(3) Å). Oxygen atoms (O1, O1^i) in the carbonyl group in the ligand were connected with protons in the bridging water molecule in another molecular unit to form a hydrogen bond (O1···O11 2.714 Å). Thus, the dimeric silver(I) complex **1** formed a supramolecular polymer structure by intermolecular hydrogen-bonding interactions, in which one coordinating water molecule plays a key role (Fig. 1b).

In **2** as shown in Fig. 2, the two units of the 3-coordinate silver(I) moiety, i.e. an $AgOP_2$ core, which consists of two PPh_3 ligands and one carboxyl oxygen atom (Ag1–O3 2.3669(16) Å, Ag1–P1 2.4157(7) Å, and Ag1–P2 2.4397(6) Å), weakly interacted intermolecularly between the silver(I) center and the carbonyl O atom (Ag1···O4^i 2.628 Å) to form a discrete centrosymmetric dimer.

The molecular structure of **3** was a mirror image of **1**. Dinuclear complex **3** was composed of two silver(I) centers with the coordinating PPh_3 ligand (Ag1–P1 2.340(3) Å) and there was a weak Ag–Ag interaction (3.294(3) Å). One carboxyl oxygen atom (O3, O3^i) in the ligand was bridged unsymmetrically between two silver(I) centers (Ag1–O3 distance 2.478(4) Å and Ag1–O3^i distance 2.356(4) Å). The oxygen atom (O11) of one water molecule was bridged symmetrically between two silver(I) centers (Ag1–O11 distance 2.450(4) Å) and the two protons participated in the hydrogen bonding interaction with the carbonyl oxygen atom of the neighboring unit (O1···O11 2.726 Å).

Complex **4** was a mirror image of **2**. The two units of the 3-coordinate silver(I) moiety (Ag1–O3 2.443(3) Å, Ag1–P1 2.425(2) Å, and Ag1–P2 2.4748(16) Å) with an $AgOP_2$ core consisting of two PPh_3 ligands and one carboxyl oxygen atom weakly interacted intermolecularly between the silver(I) center and the carbonyl oxygen atom (Ag1···O4^i 2.628 Å) to form a discrete centrosymmetric dimer.

In **5** as shown in Fig. 3a, the two units of the 2-coordinate silver(I) moiety with one PPh_3 ligand and one carboxyl oxygen atom (Ag1–O3 2.2071(18) Å and Ag1–P1 2.3543(7) Å) are linked in a manner of *head-to-tail* binding between the silver(I) center and the carbonyl O atom (Ag1–O1^i 2.506(2) Å) to form a centrosymmetric dimer. Since the dimeric complex **5** contained both *R*- and *S*-forms of the Hpyrrld$^-$ ligand in the molecule, it is a *meso*-form. Furthermore, the dimeric complex **5** in the solid state was supramolecularly arranged with van der Waals contact (Ag1···O3^{ii} 2.641 Å) as shown in Fig. 3b.

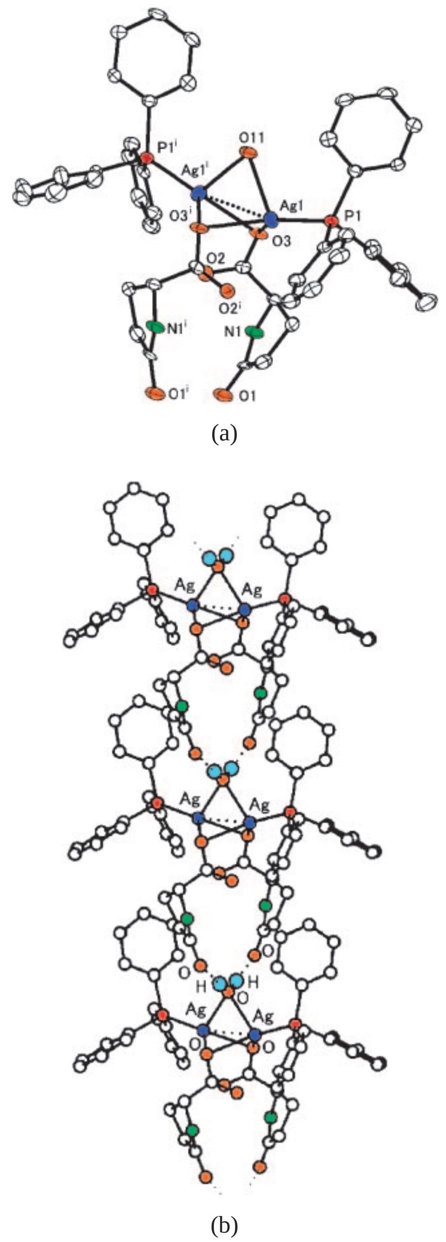
In **6** as shown in Fig. 4, the monomeric silver(I) complex

Table 2. Characterization Data of Silver(I) Complexes **1–6**

Microanalysis		Found (Calcd)/%
1	$(C_{46}H_{46}N_2P_2O_8Ag_2)$	C, 53.76 (53.51); H, 4.41 (4.49); N, 2.82 (2.71),
2	$(C_{82}H_{72}N_2P_4O_6Ag_2)$	C, 64.69 (64.75); H, 4.82 (4.77); N, 2.07 (1.84)
3	$(C_{46}H_{46}N_2P_2O_8Ag_2)$	C, 53.37 (53.51); H, 4.52 (4.49); N, 2.79 (2.71),
4	$(C_{82}H_{72}N_2P_4O_6Ag_2)$	C, 64.58 (64.75); H, 4.64 (4.77); N, 2.17 (1.84)
5	$(C_{46}H_{42}N_2P_2O_6Ag_2)$	C, 55.35 (55.44); H, 4.06 (4.25); N, 3.01 (2.81),
6	$(C_{41}H_{36}NP_2O_3Ag)$	C, 64.82 (64.75); H, 4.62 (4.77); N, 1.83 (1.84)
TG/DTA data		
1		Weight loss of 3.6% was observed below 162 °C (calcd for $2.0H_2O$, 3.4%). Endothermic peaks at 77 and 107 °C. Exothermic peaks at 182, 251, and 269 °C.
2		No weight loss before decomposition. Decomposition began around 193 °C. Endothermic peak at 219 °C. Exothermic peak at 268 °C.
3		Weight loss of 3.8% was observed below 161 °C (calcd for $2.0H_2O$, 3.4%). Endothermic peaks at 87 and 108 °C. Exothermic peaks at 185, 259, and 281 °C.
4		No weight loss before decomposition. Decomposition began around 192 °C. Endothermic peak at 217 °C. Exothermic peaks at 260 and 266 °C.
5		No weight loss before decomposition. Decomposition began around 169 °C. Exothermic peaks at 195, 267, and 286 °C.
6		No weight loss before decomposition. Decomposition began around 204 °C. Endothermic peak at 234 °C. Exothermic peak at 262 °C.
Results of molecular weight measurements in EtOH		Found (Calcd)
1		546 (1014.5 for $[Ag_2(R\text{-Hpyrrld})_2(H_2O)(PPh_3)_2]$)
2		647 (1521.1 for $[Ag(R\text{-Hpyrrld})(PPh_3)_2]$)
Some prominent IR band at 1700–400 cm^{-1} region (KBr)		
1		1656vs, 1605s, 1481m (PPh_3), 1461m, 1435s (PPh_3), 1402m, 1384m, 1330w, 1274m, 1238m, 1158w, 1097m (PPh_3), 1027w, 880w, 849w, 808w, 746m (PPh_3), 696s (PPh_3), 520m (PPh_3), 500m (PPh_3) cm^{-1}
2		1679vs, 1610m, 1590m, 1582m, 1478m (PPh_3), 1434s (PPh_3), 1393m, 1353m, 1300m, 1286m, 1254m, 1184w, 1155w, 1095m (PPh_3), 1070w, 1026m, 998w, 969w, 920w, 877w, 855w, 795w, 743m (PPh_3), 694s (PPh_3), 510m (PPh_3) cm^{-1}
3		1656vs, 1604s, 1481m (PPh_3), 1461m, 1435s (PPh_3), 1402m, 1384m, 1330w, 1274m, 1238m, 1159w, 1097m (PPh_3), 1027w, 880w, 849w, 807w, 746m (PPh_3), 696s (PPh_3), 520m (PPh_3), 500m (PPh_3) cm^{-1}
4		1679vs, 1610m, 1590m, 1582m, 1479m (PPh_3), 1434s (PPh_3), 1393m, 1353m, 1300m, 1286m, 1254m, 1184w, 1155w, 1095m (PPh_3), 1070w, 1026m, 998w, 969w, 920w, 877w, 854w, 795w, 743m (PPh_3), 694s (PPh_3), 510m (PPh_3), 484s cm^{-1}
5		1665vs, 1579s, 1480m (PPh_3), 1435m (PPh_3), 1393m, 1283s, 1098m (PPh_3), 1047w, 1027w, 997w, 926w, 878w, 748m (PPh_3), 693m (PPh_3), 620w, 545w, 521m (PPh_3), 503m (PPh_3) cm^{-1}
6		1698vs, 1589s, 1479m (PPh_3), 1432m (PPh_3), 1404m, 1298m, 1182w, 1157w, 1093m (PPh_3), 1069w, 1026w, 997w, 974w, 923w, 802w, 746s (PPh_3), 696vs (PPh_3), 516m (PPh_3), 504m (PPh_3), 493m, 441w cm^{-1}
^1H NMR		
1	(CD_2Cl_2, 23.8 °C)	δ 2.12–2.40 (4H, m, H3 and H4), 4.17 (1H, dd, H5), 7.00 (1H, s, NH), 7.39–7.50 (15H, m, Aryl).
2	(CD_2Cl_2, 24.6 °C)	δ 1.89–2.33 (4H, m, H3 and H4), 4.01 (1H, dd, H5), 5.86 (1H, s, NH), 7.31–7.44 (30H, m, Aryl).
3	(CD_2Cl_2, 23.6 °C)	δ 2.14–2.40 (4H, m, H3 and H4), 4.18 (1H, dd, H5), 6.94 (1H, s, NH), 7.39–7.51 (15H, m, Aryl).
4	(CD_2Cl_2, 22.6 °C)	δ 1.93–2.32 (4H, m, H3 and H4), 4.00 (1H, dd, H5), 5.99 (1H, s, NH), 7.31–7.44 (30H, m, Aryl).
5	(CD_2Cl_2, 24.4 °C)	δ 2.12–2.40 (4H, m, H3 and H4), 4.17 (1H, dd, H5), 6.97 (1H, s, NH), 7.39–7.51 (15H, m, Aryl).
6	(CD_2Cl_2, 23.4 °C)	δ 1.89–2.33 (4H, m, H3 and H4), 4.00 (1H, dd, H5), 5.91 (1H, s, NH), 7.31–7.43 (30H, m, Aryl).
^{13}C NMR		
1	(CD_2Cl_2, 23.4 °C)	δ 26.1 (C4), 30.8 (C3), 57.9 (C5), 129.3 (d, $J_{CP} = 10.8$ Hz, Ph), 131.1 (s, Ph), 131.1 (d, $J_{CP} = 36.5$ Hz, Ph), 134.2 (d, $J_{CP} = 15.8$ Hz, Ph), 178.6 (C6), 178.6 (C2).
2	(CD_2Cl_2, 23.5 °C)	δ 26.4 (C4), 30.9 (C3), 58.0 (C5), 129.3 (d, $J_{CP} = 9.6$ Hz, Ph), 130.8 (s, Ph), 132.6 (d, $J_{CP} = 27.8$ Hz, Ph), 134.3 (d, $J_{CP} = 17.3$ Hz, Ph), 177.7 (C6), 177.9 (C2).
3	(CD_2Cl_2, 23.4 °C)	δ 26.4 (C4), 31.1 (C3), 58.1 (C5), 129.5 (d, $J_{CP} = 10.0$ Hz, Ph), 131.3 (s, Ph), 131.4 (d, $J_{CP} = 35.7$ Hz, Ph), 134.4 (d, $J_{CP} = 16.6$ Hz, Ph), 178.7 (C6), 178.8 (C2).
4	(CD_2Cl_2, 26.1 °C)	δ 26.4 (C4), 30.9 (C3), 58.0 (C5), 129.3 (d, $J_{CP} = 9.6$ Hz, Ph), 130.7 (s, Ph), 132.7 (d, $J_{CP} = 27.8$ Hz, Ph), 134.3 (d, $J_{CP} = 16.3$ Hz, Ph), 177.7 (C6), 177.9 (C2).
5	(CD_2Cl_2, 26.0 °C)	δ 26.2 (C4), 30.9 (C3), 57.9 (C5), 129.2 (d, $J_{CP} = 10.8$ Hz, Ph), 130.9 (s, Ph), 131.5 (d, $J_{CP} = 34.0$ Hz, Ph), 134.2 (d, $J_{CP} = 16.6$ Hz, Ph), 178.3 (C6), 178.4 (C2).
6	(CD_2Cl_2, 24.6 °C)	δ 26.3 (C4), 30.8 (C3), 57.9 (C5), 129.1 (d, $J_{CP} = 9.1$ Hz, Ph), 130.5 (s, Ph), 132.5 (d, $J_{CP} = 27.4$ Hz, Ph), 134.1 (d, $J_{CP} = 16.6$ Hz, Ph), 177.4 (C6), 177.6 (C2).
^{31}P NMR		
1	(CD_2Cl_2, 22.9 °C)	δ 15.2,
2	(CD_2Cl_2, 23.5 °C)	δ 9.7,
3	(CD_2Cl_2, 22.9 °C)	δ 15.5,
4	(CD_2Cl_2, 22.9 °C)	δ 9.7,
5	(CD_2Cl_2, 23.5 °C)	δ 15.2,
6	(CD_2Cl_2, 23.4 °C)	δ 9.7,
Solid-state ^{31}P CPMAS NMR (substitution method with $(NH_4)_2HPO_4$, 23.0 °C)		
1		δ 7.23 ($J_{Ag–P}$ 699.7 Hz),
2		δ 4.23 ($J_{Ag–P}$ 669.9 Hz, $J_{P–P}$ 104.2 Hz), 8.70 ($J_{Ag–P}$ 416.8 Hz, $J_{P–P}$ 104.2 Hz),
3		δ 7.41 ($J_{Ag–P}$ 684.8 Hz),
4		δ 4.20 ($J_{Ag–P}$ 662.5 Hz, $J_{P–P}$ 104.2 Hz), 8.67 ($J_{Ag–P}$ 424.3 Hz, $J_{P–P}$ 104.2 Hz),
5		δ 8.15 ($J_{Ag–P}$ 699.7 Hz, $J_{P–P}$ 44.7 Hz),
6		δ 4.84 ($J_{Ag–P}$ 387.1 Hz, $J_{P–P}$ 148.9 Hz), 8.24 ($J_{Ag–P}$ 439.2 Hz, $J_{P–P}$ 134.0 Hz)

with AgO_2P_2 core (Ag1–P1 2.436(3) Å, Ag1–P2 2.432(2) Å, Ag1–O2 2.529(7) Å, Ag1–O3 2.399(7) Å, Ag2–P3 2.441(3) Å, Ag2–P4 2.410(2) Å, Ag2–O5 2.369(7) Å, and Ag2–O6 2.508(8) Å) was formed with a chelation by the two carboxyl oxygen atoms and the two monodentate PPh_3 ligands. The bond angles around the silver(I) center, e.g. P1–Ag1–P2 125.79(9)°, O2–Ag1–O3 53.2(2)°, indicate an extraordinarily distorted tetrahedral geometry. The carbonyl oxygen atom did not interact with any other groups. In the unit cell ($Z = 2$), a combination of one *R*-complex and one *S*-complex was contained as a racemic compound.

Classification of the Ag–O Bonding Modes. Complexes **1–6** and the silver(I) precursors were classified to four types (Type I–IV) based on the Ag–O bonding modes formed among



(a)

(b)

Fig. 1. (a) Molecular structure of the local coordination around silver(I) center of $[Ag_2(R\text{-}Hpyrrld)_2(H_2O)(PPh_3)_2]$ (**1**) with 50% probability ellipsoids (symmetry operation $i = x - y, -y, -z + 1/3$), and (b) side view of the polymer chains extended along the crystallographic a axis.

the silver center, and the carboxyl and/or carbonyl as shown in Fig. 5. Complexes belonging to the Type I are formed by monodentate coordination of the single oxygen atoms to the silver(I) center as observed in **2**, **4**, and **5**, that in the Type II is formed by a chelate formation of the two carboxyl oxygen atoms as observed in **6**, those in the Type III are formed by bridging of the single oxygen atoms between two silver(I) centers as observed in **1** and **3**, and those in the Type IV are obtained by bis(carboxylato-*O*,*O*′)-bridged dimer (Ag_2O_4 core) formation as observed in the precursors without PPh_3 ligand. The Ag–O bonding modes in **1**–**6** were quite different, which strongly depended upon both chirality of the $Hpyrrld^-$ ligand and the number of coordinating PPh_3 ligands.

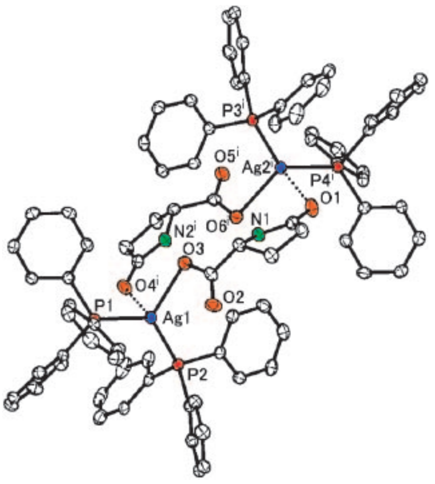
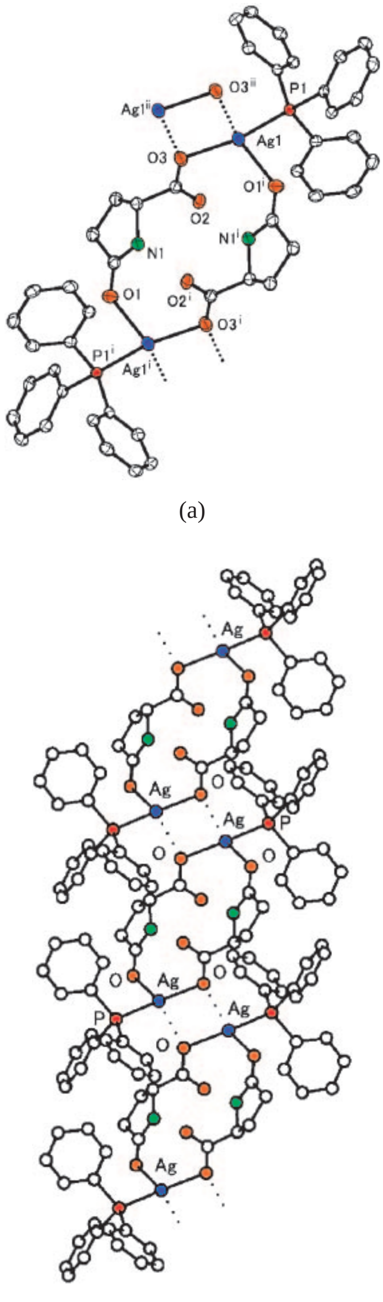


Fig. 2. Molecular structure of the local coordination around silver(I) center of $[Ag(R\text{-}Hpyrrld)(PPh_3)_2]_2$ (**2**) with 50% probability ellipsoids (symmetry operation $i = x + 1, y, z$).

Reactivities of Complexes. The reaction from **1** and **3** producing the dimeric *meso*-form **5**, which includes a ligand-exchange process, was confirmed. On the other hand, the racemization reaction from **2** and **4** producing **6** was also found. The latter reaction does not include a ligand exchange process, but only a change of the bridging $Hpyrrld^-$ ligand between two silver(I) centers to the chelating ligand to the single silver(I) atom. Interestingly, complex **2** or **4** alone did not show such a chelation: in the presence of **4**, the bridging $Hpyrrld^-$ ligand in **2** was changed to a chelated ligand, and in the presence of **2**, that in **4** was changed to a chelated ligand. Thus, complex **6** is a racemic compound composed of a combination of *R*- and *S*-complexes, both of which take an extraordinarily distorted tetrahedral geometry. Probably, this racemization reaction would be caused in place of a formation of the unstable "*meso*" form of dinulcear silver(I) complex with two PPh_3 ligands.

These complexes (**1**, **5**, and probably **3**) were antimicrobially active, while complexes (**2**, **6**, and probably **4**) were inactive, as described later.

Behavior in EtOH, (^{31}P, ^{1}H, and ^{13}C) NMR in CD_2Cl_2, and Solid-State ^{31}P NMR Spectroscopy. Solution molecular weight measurements of **1** (found 546; calcd 1014.5 for the formula without hydrated water) and **2** (found 647; calcd 1521.1) in EtOH indicate that these complexes are present as a monomeric species due to complete dissociation equilibrium. If the dimeric complex **1** is dissociated by dissociation degree $\alpha = 1$, several monomeric species containing EtOH coordination, e.g., "$[Ag(R\text{-}Hpyrrld)(PPh_3)(EtOH)_n]$" (FW 544.3 for $n = 1$; 590.4 for $n = 2$) can be reasonably postulated in solution. On the other hand, for the dimeric complex **2**, not only the complete dissociation to the monomer "$[Ag(R\text{-}Hpyrrld)(PPh_3)_2]$" (FW 760.6), but also the dissociation of the PPh_3 ligand to the species such as "$[Ag(R\text{-}Hpyrrld)(PPh_3)(EtOH)_n]$" should be also taken into account. If the complete dissociation degree ($\alpha = 1$) to the monomer can be assumed, the dissociation degree of the PPh_3 ligand can be evaluated as 0.176 from the found and calculated molecular weights. Using these values, the distribution of dissociation species of **2** is estimated



(a)

(b)

Fig. 3. (a) Molecular structure of the local coordination around silver(I) center of $\{[\mathrm{Ag}(R,S\text{-Hpyrrld})(\mathrm{PPh_3})]_2\}_n$ (**5**) with 50% probability ellipsoids (symmetry operation $i = -x+1,\ -y,\ -z$; $ii = -x+2,\ -y,\ -z$). The dimeric complex is a *meso*-form with both one *R*- and one *S*-Hpyrrld$^-$ ligands in the molecule. (b) Side view of the polymer chains extended along the crystallographic *a* axis.

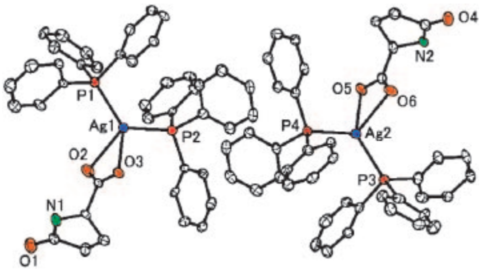


Fig. 4. Molecular structure of the local coordination around silver(I) center of $[\mathrm{Ag}(R,S\text{-Hpyrrld})(\mathrm{PPh_3})_2]$ (**6**) with 50% probability ellipsoids. In the unit cell, a racemic mixture of the enantiomeric complexes was found.

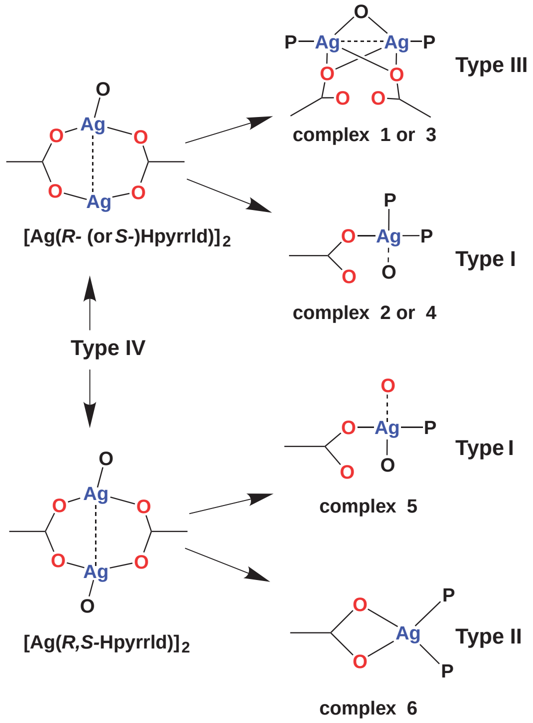


Fig. 5. Classification (Type I–IV) of the precursor $[\mathrm{Ag(Hpyrrld)}]_2$ and complexes **1**–**6** based on the Ag–O bonding modes among the silver center, and the carboxyl and/or carbonyl oxygen atoms.

to be the monomeric silver(I) species having two $\mathrm{PPh_3}$ ligands (70.0%), the species having one $\mathrm{PPh_3}$ ligand (15.0%), and free $\mathrm{PPh_3}$ (15.0%).

Thus, the molecular formulas and molecular structures of **1**–**4** are valid only in the solid state. Although the solvent used for NMR measurements is different from that of molecular weight measurements, solution (^{31}P, ^{1}H, and ^{13}C) NMR in $\mathrm{CD_2Cl_2}$ should be understood based on the monomeric species. This is the case for complexes **5** and **6**.

The ^{31}P NMR spectra in $\mathrm{CD_2Cl_2}$ (Table 2) showed only one resonance at around δ 15.2 for silver(I) complexes (**1**, **3**, and **5**) with one $\mathrm{PPh_3}$ ligand per silver(I) atom and only one resonance at around δ 9.7 for silver(I) complexes (**2**, **4**, and **6**) with two $\mathrm{PPh_3}$ ligands per silver(I) atom. Since no ^{31}P signal of the free $\mathrm{PPh_3}$ (-5.33 ppm) ligand is observed in the ^{31}P NMR spectra of **2**, **4**, and **6** at room temperature in $\mathrm{CD_2Cl_2}$, the observed spectra should result from a rapid dynamic exchange of the free $\mathrm{PPh_3}$ ligands as dissociation species. In $\mathrm{CD_2Cl_2}$ solution, the dimeric complex **5** with *meso*-form is changed to a racemic mixture of monomeric *R*- and *S*-complexes with one $\mathrm{PPh_3}$ ligand per silver(I) atom. Solution ^{31}P NMR also indicates that the racemic compound **6** in the solid state will be

Table 3. Selected Bond Distances (Å) and Angle (°) for Silver(I) Complexes **1–6**

1		**2**		**3**		**4**		**5**		**6**	
Ag1–O3	2.465(3)	Ag1–O3	2.3669(16)	Ag1–O3	2.478(4)	Ag1–O3	2.443(3)	Ag1–O3	2.2071(18)	Ag1–O2	2.529(7)
Ag1–O3^{i}	2.341(3)	Ag1–P1	2.4157(7)	Ag1–O3^{i}	2.356(4)	Ag1–P1	2.425(2)	Ag1–O1^{i}	2.506(2)	Ag1–O3	2.399(7)
Ag1–O11	2.438(3)	Ag1–P2	2.4397(6)	Ag1–O11	2.450(4)	Ag1–P2	2.4748(16)	Ag1–P1	2.3543(7)	Ag1–P1	2.436(3)
Ag1–P1	2.3312(10)	Ag2^{i}–O6^{i}	2.4420(16)	Ag1–P1	2.340(3)	Ag2^{i}–O6^{i}	2.367(3)	Ag1···O3^{ii}	2.641	Ag1–P2	2.432(2)
Ag1···Ag1^{i}	3.2854(7)	Ag2^{i}–P3^{i}	2.4715(6)	Ag1···Ag1^{i}	3.294(3)	Ag2^{i}–P3^{i}	2.4398(16)			Ag2–O5	2.369(7)
O1···O11	2.714	Ag2^{i}–P4^{i}	2.4219(7)	O1···O11	2.726	Ag2^{i}–P4^{i}	2.423(2)			Ag2–O6	2.508(8)
		Ag1···O4^{i}	2.628			Ag1···O4^{i}	2.628			Ag2–P3	2.441(3)
		Ag2^{i}···O1	2.616			Ag2^{i}···O1	2.639			Ag2–P4	2.410(2)
P1–Ag1–O3^{i}	144.60(7)	O3–Ag1–P1	114.94(4)	P1–Ag1–O3^{i}	144.97(9)	O3–Ag1–P1	124.18(9)	O1^{i}–Ag1–O3	106.01(7)	O2–Ag1–P1	115.4(2)
P1–Ag1–O11	117.91(7)	O3–Ag1–P2	116.00(4)	P1–Ag1–O11	117.68(9)	O3–Ag1–P2	105.38(9)	O1^{i}–Ag1–P1	94.82(5)	O2–Ag1–P2	110.0(2)
O3^{i}–Ag1–O11	79.00(8)	P1–Ag1–P2	129.05(2)	O3^{i}–Ag1–O11	79.13(11)	P1–Ag1–P2	130.28(4)	O3–Ag1–P1	155.11(6)	O2–Ag1–O3	53.2(2)
P1–Ag1–O3	131.59(7)	O6^{i}–Ag2^{i}–P3^{i}	105.54(4)	P1–Ag1–O3	130.9(9)	O6^{i}–Ag2^{i}–P3^{i}	116.12(9)			O3–Ag1–P1	106.2(2)
O3^{i}–Ag1–O3	80.71(10)	O6^{i}–Ag2^{i}–P4^{i}	124.07(4)	O3^{i}–Ag1–O3	81.05(13)	O6^{i}–Ag2^{i}–P4^{i}	114.78(9)			O3–Ag1–P2	124.54(19)
O11–Ag1–O3	76.66(8)	P4^{i}–Ag2^{i}–P3^{i}	130.24(2)	O11–Ag1–O3	76.83(10)	P4^{i}–Ag2^{i}–P3^{i}	129.09(5)			P1–Ag1–P2	125.79(9)
P1–Ag1–Ag1^{i}	163.68(3)			P1–Ag1–Ag1^{i}	163.35(4)					O5–Ag2–P3	107.0(2)
O3^{i}–Ag1–Ag1^{i}	48.47(6)			O3^{i}–Ag1–Ag1^{i}	48.61(10)					O5–Ag2–P4	123.7(2)
O11–Ag1–Ag1^{i}	47.64(6)			O11–Ag1–Ag1^{i}	47.75(8)					O5–Ag2–O6	54.0(2)
O3–Ag1–Ag1^{i}	45.32(6)			O3–Ag1–Ag1^{i}	45.51(8)					O6–Ag2–P3	117.1(2)
Ag1–O3–Ag1^{i}	86.28(8)			Ag1–O3–Ag1^{i}	85.88(12)					O6–Ag2–P4	108.5(2)
Ag1–O11–Ag1^{i}	84.73(13)			Ag1–O11–Ag1^{i}	84.50(16)					P3–Ag2–P4	125.62(8)

present as a racemic mixture of the monomeric complexes with a very similar geometry to those of **2** and **4** in solution, which would contain the monodentate coordination of the Hpyrrld^{-} ligand, but not the chelation. The resonances in complexes **1–6** were observed in much higher field than that of one coordinating PPh_3 to the gold(I) center (δ 28.0 for $[Au(R,S\text{-Hpyrrld})(PPh_3)]$,[6g] δ 29.4 for $[Au(O_2CNEt_2)(PPh_3)]$[8] ($O_2CNEt_2{}^{-} = N,N'$-diethylcarbamato)).

The solid-state ^{31}P CPMAS NMR spectra of **1–6** (Table 2), which were quite different from the solution ^{31}P NMR spectra, showed signals of the PPh_3 ligand coordinating to the silver(I) atom as doublet peaks (two lines) for **1** and **3**, as two double doublet peaks (six lines) for **2**, **4**, and **6** and as double doublet peaks (four lines) for **5**. These splitting peaks are due to ^{1}J(Ag–P) and ^{2}J(P–P) couplings,[9] and these results are consistent with the solid-state structures revealed by X-ray crystallography.

The ^{1}H NMR spectra of **1–6** in CD_2Cl_2 (Table 2) showed signals of the coordinating Hpyrrld^{-} ligands as multiplet peaks for the two methylene groups (H4 and H3), as single peak for the NH proton and as double doublet peaks (four lines) for the H5 proton within the ring. The ^{13}C NMR spectra of **1–6** in CD_2Cl_2 (Table 2) showed signals of the coordinating Hpyrrld^{-} ligands as single peaks for C4, C3, C5, C6, and C2.

Antimicrobial Activities. Antimicrobial activities estimated as the minimum inhibitory concentration (MIC, μg mL^{-1}) for complexes **1**, **2**, **5**, and **6** are listed in Table 4.

Antimicrobial activites of "free ligand" H_2pyrrld were estimated as >1000 μg mL^{-1} for tested bacteria, yeast, and molds, showing no activity.[6b] The precursor without PPh_3 ligand, $[Ag(R\text{-Hpyrrld})]_2$, showed a wide spectrum of remarkable and excellent activities against selected Gram-negative (*E. coli* and *P. aeruginosa*) and -positive bacteria (*B. subtilis* and *S. aureus*) and yeast (*C. albicans* and *S. cerevisiae*), and even against two tested molds (*A. niger* and *P. citrinum*).[6b] The enantiomeric complex $[Ag(S\text{-Hpyrrld})]_2$ has also shown very similar antimicrobial spectrum and activities, suggesting that the chirality of the complexes does not affect the antimicrobial activities.[6a]

Complex **1** with one PPh_3 ligand per silver(I) atom showed a relatively wide spectrum with effective activities against bacteria and yeast. Complex **1** also showed activity against one (*P. citrinum*) of two tested molds. Complex **5** with one PPh_3 ligand per silver(I) atom also showed effective activities against Gram-negative (*E. coli*) and -positive bacteria (*B. subtilis* and *S. aureus*) and yeast (*C. albicans* and *S. cerevisiae*), and even against two tested molds (*A. niger* and *P. citrinum*). On the other hand, complexes **2** and **6** with two PPh_3 ligands per silver(I) atom showed no activity against all microorganisms tested. Complexes **1** and **3** which showed a ligand-exchange process, and the resulting, still labile complex **5** were antimicrobially active, whereas complexes **2** and **4** which did not show the ligand-exchange process and the inert complex **6** were antimicrobially inactive. These aspects are consistent with the previously reported conclusions.[6]

The antimicrobial activities observed here were significantly correlated with the number of soft PPh_3 ligands per silver(I) atom contained in the complexes and, therefore, with the resulting Ag–O bonding modes.

Table 4. Antimicrobial Activities of Silver(I) Complexes **1**–**6**, $[Ag(R\text{-}Hpyrrld)]_2$ and "Free" Ligand Evaluated by Minimum Inhibitory Concentration (MIC/µg mL^{-1})

	R-H_2pyrrld[a)]	**1**	**2**	**5**	**6**	$[Ag(R\text{-}Hpyrrld)]_2$[a)]
Escherichia coli	>1000	62.5	>1000	125	>1000	15.7
Bacillus subtilis	>1000	62.5	>1000	500	>1000	31.3
Staphylococcus aureus	>1000	125	>1000	125	>1000	31.3
Pseudomonas aeruginosa	>1000	250	>1000	1000	>1000	15.7
Candida albicans	>1000	500	>1000	62.5	>1000	7.9
Saccharomyces cerevisiae	>1000	500	>1000	62.5	>1000	15.7
Aspergillus niger	>1000	>1000	>1000	250	>1000	15.7
Penicillium citrinum	>1000	250	>1000	250	>1000	15.7

a) Ref. 6b.

Conclusion

The crystal and molecular structures of six chiral or racemic triphenylphosphinesilver(I) carboxylate complexes, $[Ag_2(R\text{-}Hpyrrld)_2(H_2O)(PPh_3)_2]\cdot H_2O$ (**1**), $[Ag(R\text{-}Hpyrrld)(PPh_3)_2]_2$ (**2**), their enantiomers **3** and **4**, respectively, $\{[Ag(R,S\text{-}Hpyrrld)(PPh_3)]_2\}_n$ (**5**), and $[Ag(R,S\text{-}Hpyrrld)(PPh_3)_2]$ (**6**) were determined. In the solid state, complex **1** having one PPh_3 ligand per silver(I) atom was a polymer formed by supramolecular arrangement of the dimeric unit $[Ag(Hpyrrld)(PPh_3)]_2$. In **1**, the two protons of one coordinating water molecule bridged between two silver(I) atoms with Ag–Ag interaction (3.2854(7) Å) significantly contributed to a formation of the intermolecular hydrogen bonds with the carbonyl groups of the $Hpyrrld^-$ ligands in the neighboring unit. The dimeric complex **2** having two PPh_3 ligands per silver(I) atom was a discrete centrosymmetric dimer of two AgP_2O(carboxyl)-O(carbonyl) units, while the dimeric complex **5** having one PPh_3 ligand per silver(I) atom was a *meso*-form of *R*- and *S*-ligands, the dimeric units of which were further supramolecularly arranged with van der Waals contact ($Ag1\cdots O3^{ii}$ 2.641 Å) in the solid state. Complex **6** was a racemic compound of *R*- and *S*-complexes, each of which was a 4-coordinate monomer composed of a chelation with two carboxyl oxygen atoms and two PPh_3 ligands.

The Ag–O bonding modes in these silver(I) complexes were different and were dependent upon both chirality of the $Hpyrrld^-$ ligand and the number of PPh_3 ligands. Complexes **1**–**6** prepared here and the dimeric silver(I) precursors were classified to four types (I–IV) based on the Ag–O bonding modes formed among the silver(I) center, and the carboxyl and/or carbonyl oxygen atoms in the $Hpyrrld^-$ ligand. Formation of dimeric *meso*-form complex **5** from **1** and **3**, and racemization from **2** and **4** producing **6** were also found. Solution molecular weight measurements, solution and solid-state ^{31}P NMR revealed that solution structures of **1**–**6** and their behaviors in solution were quite different from those in the solid state. Explicit correlation of the antimicrobial activities with the number of soft PPh_3 ligands per silver(I) atom was found.

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