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Disilver(I) Coordination Complexes: Synthesis, Reaction Chemistry, and Their Potential Use in CVD and Spin-Coating Processes for Silver Deposition

Alexander Jakob,^[a] Tobias Rüffer,^[a] Heike Schmidt,^[a] Patrice Djiele,^[a] Kathrin Körbitz,^[a] Petra Ecorchard,^[a] Thomas Haase,^[b] Katharina Kohse-Höinghaus,^[b] Swantje Frühauf,^[c] Thomas Wächtler,^[c] Stefan Schulz,^[c] Thomas Gessner,^[c] and Heinrich Lang^{*[a]}

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The synthesis of complexes $[Aq_2X] [X = O_2CCO_2 (3a), C_4O_4]$ $(\mathbf{3b})_1$, $O_2CCH_2CO_2$, $(\mathbf{3c})_1$, $O_2C(CH_2)_2CO_2$, $(\mathbf{3d})_1$, cis- $O_2CCH=$ CHCO₂ (3e), trans-O₂CCH=CHCO₂ (3f), para-O₂CC₆H₄CO₂ (3g)] and $[(R_3P)_m AgXAg(PR_3)_m]$ [R = Ph, X = C₄O₄, m = 2 (10a), m = 3 (10b); R = nBu, $X = O_2CCH_2CO_2$, m = 2 (10c), m= 3 (10d); X = $O_2C(CH_2)_2CO_2$, m = 1 (10e), m = 2 (10f), m = 3 (10g); $X = cis-O_2CCH=CHCO_2$, m = 1 (10h), m = 2 (10i), m $= 3 (10j); X = trans-O_2CCH=CHCO_2, m = 1 (10k), m = 2 (10l),$ m = 3 (**10m**); X = *para*-O₂CC₆H₄CO₂, m = 2 (**10n**)] is reported. Compoundds 3a-3g are accessible by the reaction of $[AqNO_3]$ (1) with H₂X (2a-2g), while 10a-10n can be prepared by treatment of 3a-3q with PR_3 (9a, R = Ph; 9b, R =*n*Bu) in the ratios of 1:2, 1:4, or 1:6. When $[{Ag(bipym)(NO_3)} \cdot$ H_2O_{n} (6) (bipym = bipyrimidine) reacts with (HNEt₃)₂- (O_2CCO_2) (7), [{Ag(bipym)Ag(O_2CCO_2)·4H_2O}_n] (5) and $[{(bipym)(Ag(O_2CCO_2H))_2}_n]$ (8) are formed. The molecular structures for 5, 6, and 8 in the solid state are reported. For

Introduction

Dicarboxylic acids and squaric acid (3,4-dihydroxycyclobut-3-ene-1,2-dione) have been well known for quite some time, and hence, there exists a versatile number of literature reports on their synthesis, reaction chemistry, structures, and ligand properties.^[1] Recently, dicarboxylates became of considerable interest in transition-metal coordination chemistry because they can act as planar bridging units between metal centers, to form homo- or heterodimetallic or even two- and three-dimensional polymeric structures for molecular recognition.^[2] Such modular constructed assemblies may be used as representative model compounds in the fundamental study of electron-transfer

- [b] Universität Bielefeld, Physikalische Chemie I, Postfach 100131, 33501 Bielefeld, Germany
- [c] Technische Universität Chemnitz, Fakultät für Elektrotechnik und Informationstechnik, Zentrum für Mikrotechnologien, Reichenhainerstr. 70, 09126 Chemnitz, Germany

5, the formation of a 3D network is characteristic, in which 1D chains of $\{Aq(bipym)Aq(O_2CCO_2)\}_n$ interact with each other through π - π interactions between the bipym ligands to extend in one direction, while H₂O molecules act as connectivities thorugh the intermolecular H-bridge formation to extend in the other direction. Polymeric 6 consists of 2D layers formed by individual 1D chains of $\{Aq(bipym)Aq(bipym)\}_n$ with $\pi - \pi$ interactions between the bipym ligands. In **8**, {(HO₂CCO₂)Ag(bipym)Ag(O₂CCO₂H)} units undergo intermolecular H-bridge formation to create 2D layers, π - π interactions between individual bipym ligands produce a 3D network. The use of **10d** as a CVD precursor in the deposition of Ag on glass by using a direct liquid injection system is discussed. The Ag films show a rough appearance and contain C impurities. The use of **10e** and **10f** as spin-coating precursors for the deposition of Ag on TiN-coated oxidized Si wafers is reported.

or photo-induced energy-transfer processes.^[3] In addition, they offer diverse applications in the field of new materials, e.g., smart system integration, and they can be used as materials for micro- and nanosystems, nanostructures, and devices.^[4]

CVD (chemical vapor deposition), ALD (atomic layer deposition), and spin-coating processes are considered to be alternatives for or supplementing technologies to, e.g., PVD (physical vapor deposition) and electrochemical metal deposition procedures for use in future technology areas for the fabrication of micro- and nanoelectronics.^[5]

In this context, silver as a noble metal exhibits the lowest resistivity and highest thermal conductivity of all metals.^[6] For this reason, the design of silver(I) coordination complexes is of potential interest because they are promising candidates for the deposition of thin silver films on different substrates. Lately, there have been some reports on the synthesis of novel volatile phosphane and phosphite silver(I) carboxylates and their use as CVD precursors for the deposition of silver on different (structured) wafer materials.^[1b,7] Additional silver(I) metal–organic complexes that can successfully be applied as MOCVD precursors include L_mAg carboxylates, $L_mAg \beta$ -diketonates, and $R_3PAgC_5H_5$ (R =



 [[]a] Technische Universität Chemnitz, Fakultät für Naturwissenschaften,
 Institut für Chemie, Lehrstuhl für Anorganische Chemie, Straße der Nationen 62, 09111 Chemnitz, Germany
 Fax: +49-371-531-21219
 E-mail: heinrich.lang@chemie.tu-chemnitz.de

alkyl, aryl; L = trialkyl-/triarylphosphane, alkene, diene, bipyridine; m = 1, 2, 3).^[7] The gas-phase decomposition behavior of such compounds was studied by applying temperature-programmed and in situ mass spectrometry.^[8]

We report here on the synthesis of disilver(I) dicarboxylates and on the related species thereof. The use of selected samples for metal deposition is discussed.

Results and Discussion

Syntheses and Characterization of Disilver Carboxylates

The synthesis of the Lewis base disilver(I) dicarboxylates and squarates 5, 8, and 10a-10n (Lewis base = phosphane, phosphite, bipyrimidine) (reactions 1-3, Table 1 and Table 4) requires the accessibility of the appropriate silver salts $[Ag_2X]$ (3a–3g), which can easily be prepared by reacting 2 equiv. $[AgNO_3]$ (1) with the dicarboxylic and squaric acids H_2X [H_2X = oxalic acid (2a), squaric acid (2b), malonic acid (2c), succinic acid (2d), maleic acid (2e), fumaric acid (2f), terephthalic acid (2g)] in a mixture of ethanol/acetonitrile (30:1, v/v) in the presence of NEt₃ at ambient temperature [Reaction (1)]. The silver salts $[Ag_2X]$ $[X = O_2 CCO_2 (3a),^{[1b,9a]} C_4 O_4 (3b),^{[9b]} O_2 CCH_2 CO_2 (3c),^{[9c]}$ $O_2C(CH_2)_2CO_2$ (3d),^[9d] cis- $O_2CCH=CHCO_2$ (3e),^[9e] trans- $O_2CCH=CHCO_2$ (**3f**),^[9f] para- $O_2C-C_6H_4-CO_2$ (**3g**)]^[9g] precipitate as colorless or off-white to pale yellow solids, while [HNEt₃]NO₃ remains in solution. After decanting the supernatant solution and washing the residue thoroughly with cold ethanol and then with petroleum ether, 3a-3g were obtained in the analytically pure form and in high yield (see Experimental Section and Table 1).

Table 1. Synthesis of the silver salts [Ag₂X] (3a-3g).

Compound	Х	Yield ^[a] [%]	Refs.
3a	O ₂ CCO ₂	96	[1b,9a]
3b	$C_4 O_4 [b]$	87	[9b]
3c	O ₂ CCH ₂ CO ₂	90	[9c]
3d	$O_{2}C(CH_{2})_{2}CO_{2}$	85	[9d]
3e	cis-O ₂ CCH=CHCO ₂	90	[9e]
3f	trans-O ₂ CCH=CHCO ₂	98	[9f]
3g	para-O ₂ CC ₆ H ₄ CO ₂	95	[9g]

[a] On the basis of 2a-2g. [b] $C_4O_4 =$ squarate.

The silver salts 3a-3g are very stable species with the exception of 3b, which decomposes within days at ambient temperature. Thus, they should best be stored at -30 °C to prevent decomposition.

The low solubility of 3a-3g is associated with the aggregated structural form of these assemblies.^[9] To obtain soluble materials the oligo- or polymeric structures of these metal-organic compounds must be broken to produce lower aggregated or even monomolecular species. This can be achieved by the addition of Lewis bases. Thus, complex **3a** was treated with bipyrimidine (bipym) (4) in a 1:1 molar ratio in chloroform at 25 °C. However, this reaction formed a coordination polymer with the composition [(bipym)Ag- $(O_2CCO_2)Ag_n$ (5). Because of the low basicity of bipym only small amounts of 5 could be isolated. A more efficient synthesis methodology to prepare 5 is the reaction of [(bipym)AgNO₃] (6)^[11] with the ammonium salt [HNEt₃]₂- $[O_2CCO_2]$ (7) [Reaction (2)]. It was found that the highest yield is obtained when 7 was used in a twofold excess (Experimental Section). After appropriate workup, polymeric 5 could be isolated as a pale yellow solid. The disilver coordination complex 8 was formed as a side product in which the bipym building block connects two Ag(O₂CCO₂H) building blocks [Reaction 2, Experimental Section].

The identity of **5** was confirmed by elemental analysis and IR spectroscopy. The molecular structures of **5**, **6**, and **8** in the solid state were additionally solved by single X-ray structure analysis, thus confirming the structural assignments made from spectroscopic analysis.

Most characteristic in the IR spectra of $5^{[10]}$ and 8 are their \tilde{v}_{CO} , $\tilde{v}_{C=C}$ and $\tilde{v}_{C=N}$ vibrations found between 1312– 1701 cm⁻¹, the \tilde{v}_{CH} vibrations at 3044 and 3064 cm⁻¹, respectively, and the broad \tilde{v}_{OH} absorption at 3368 (5) and 3448 cm⁻¹ (8) from the crystal water that is part of the hydrogen-bonded network (Figures 1, 3, Figures 6, 8, vide infra). For complex **6**, a very strong absorption band at 1384 cm⁻¹ is observed which proves the presence of a nitrate anion,^[11] and hence points to a polymeric structure as partly evidenced by conductivity measurements.^[12]

The molecular structures of **5**, **6**, and **8** in the solid state were established by single X-ray crystallographic studies (Figures 1–8). Suitable crystals were obtained by slow concentration of water solutions containing the appropriate transition-metal complexes at ambient temperature. ORTEP diagrams, selected bond lengths (Å) and angles (°) are given in Figures 1–8 as well as in Tables 2 and 3, while the crystal and structure refinement data are presented in Table 5 (Experimental Section).



Complex 5 crystallized in the centrosymmetric space group $P\bar{1}$ to form a 3D network consisting of 1D coordination polymers with repeating units {Ag(bipym)Ag-(O₂CCO₂)}_n, in which the bipyrimidine building blocks and the oxalato anions act as flexidentate alternating ligands. Within the 1D coordination polymer the alternating {Ag(O₂CCO₂)Ag} and {Ag(bipym)Ag} metal-organic moieties, which consist of the atoms Ag1, Ag1b, O1, O2, O1b, O2b, C5, C5b (unit I) and Ag1b, Ag1c, N1c, N2c, N1b, N2b, C1c-C4c, C1b-C4b (unit II), respectively, are planar as determined from the calculation of mean planes (unit I: r.m.s.d. = 0.021 Å, unit II: r.m.s.d. = 0.058 Å) (r.m.s.d. = root means square deviation) (Figure 1). The 1D coordination polymer is planar as the dihedral angle between units I and II is 6.3°.



Figure 1. ORTEP diagram (50% probability level) of a part of the 1D strain formed by 5 in the solid state. All hydrogen atoms, except for the O-bonded hydrogen atoms, have been omitted for clarity. Labels "a-c" refer to atoms of the first to the third symmetrygenerated asymmetric unit of 5. Selected distances (Å) and angles (°): Ag1-O1 2.2957(17), Ag1-N1 2.336(2), Ag1-N2a 2.421(2), Ag1-O2b 2.4810(19), C1-C1a 1.505(5), C5-C5a 1.575(5); O1-Ag1-N1 126.94(7), O1 Ag1-N2a 161.19(7), N1-Ag1-N2a 70.08(8), O1-Ag1-O2b 69.39(6), N1-Ag1-O2b 163.63(7), N2a-Ag1-O2b 93.61(7), C1-N1-Ag1 118.22(17), C2-N1-Ag1 124.42(17), Č1-N2-Ag1 115.92(17), C4a-N2a-Ag1 127.00(17), C5-O1-Ag1 121.09(16), C5–O2b–Ag1 114.80(16).

The silver(I) ion possesses an intrachain coordination number of 4 and the bipym and oxalate ligands are chelatebonded to the group 11 metal ion, which results in a distorted square-planar geometry around the silver atom (r.m.s.d. deviation from planarity of the AgN_2O_2 atoms 0.08 Å). The cis angles are 69.39(6) (O1-Ag1-O2b) and 126.94(7)° (O1-Ag1-N1), while the trans angles are 161.19(7) (O1-Ag1-N2a) and 163.63(7)° (N1-Ag1-O1b). The water molecules are hydrogen-bonded to all four oxalate oxygen atoms (Figure 2, Table 2), with bond numbers I and II. The remaining water hydrogen atoms also form intermolecular hydrogen bonds and create a 3D network structure (Figures 2 and 3). As shown in Figure 2, the water molecules are bonded to each other through hydrogen bond number III (Table 2) and connect to form 1D chains superimposed on each other. Between these superimposed 1D chains $\pi - \pi$ interactions are additionally observed between the bipym and oxalate moieties as well as short Ag. O interchain distances of 2.817(2) Å (Figure 2). As shown in Figure 2, an Ag…O interchain contact is observed between two adjacent 1D chains only but not between the superim-



posed 1D chains. Eventually, the silver(I) ions possess a coordination number of 5 in a distorted square-pyramidal N_2O_3 coordination setup.



Figure 2. Graphical representation of the connection of 1D chains of **5** in the crystal structure induced by π - π interactions between bipym and oxalate ligands, <) refers to the interplanar angle, *d* gives the shortest distance of interacting π -conjugated units, the intermolecular hydrogen bonds and interchain Ag···O contacts are shown. Labels "a-i" refer to the first to the ninth symmetry-generated asymmetric unit of **5**. All hydrogen atoms, except for the Obonded ones, have been omitted for clarity.

Table 2. Intermolecular hydrogen bond lengths (Å) and angels (°) within the molecular structure of 5.^[a]

No.	D–H	А	D····A	D–H•••A
Ι	O3–H10	01	2.868(3)	159(4)
II	O4–H3o	O2a	2.763(3)	167(3)
III	O3–H2o	O4[a]	2.762(4)	165(4)
IV	O4–H4o	O3a	2.773(4)	172(7)

[a] I-IV = number of the hydrogen-bridging bond; D = donor, A = acceptor.

As can be seen from Figure 3, the hydrogen atoms labeled with H4o and symmetry-related hydrogen atoms are not involved in the formation of 2D layers. It is these hydrogen atoms that are responsible for the connection between the 2D layers to form an overall 3D network through intermolecular hydrogen bond number IV (Table 2). A representative part of the 3D network is shown in Figure 3.

Recently, the crystal structure of a chemically identical compound was reported, denoted as $[Ag_2(\mu_2-bpm)(\mu_2-ox)]_n$ · $4nH_2O$ (**5a**).^[10] While the synthesis of **5a** differs from that of **5**, the structural features of both compounds are certainly identical, although **5a** crystallizes in a different centrosymmetric $P\overline{1}$ unit cell when compared with **5**. All bond lengths and angles of **5** are similar to those of **5a**. Furthermore, it should be noted that the silver(I) ions in **5a** do have, as observed for **5**, an interchain coordination number of 5 in a distorted square-pyramidal N₂O₃ coordination environment, but they do not possess a distorted N₂O₄ geometry, as reported. In addition, **5a** forms, as observed for **5**, a 3D network and not a "quasi two-dimensional (2D) network", as reported.

Complex **6** crystallizes in the noncentrosymmetric orthorhombic space group $Pna2_1$. The asymmetric unit of **6** consists of two silver atoms, two bipym moieties, two nitrate anions, and one water molecule (Figure 4). 2D layers of individual 1D coordination polymers with the repeating unit



Figure 3. Top (left) and side view (right) of the 3D network structure formed by 5 in the solid state. Labels "a-i" refer to the first to the ninth symmetry-generated asymmetric unit of 5. All hydrogen atoms, except for the O-bonded ones, have been omitted for clarity.

 $\{Ag(bipym)Ag(bipym)\}_n$ are formed, which are connected through π - π interactions between adjacent bipym moieties (Figures 4 and 5). As shown in Figure 4, a nitrate ion is weakly bonded to one of the two crystallographically independent silver ions (Ag1) (d(Ag1-O6) = 2.958 Å), as the sum of the van der Waals radii of silver(I) and oxygen is 3.24 Å.^[13] Furthermore, a water molecule is hydrogen bonded to both a coordinated and a noncoordinated nitrate anion (Table 3).

Within the 1D coordination polymer, the {Ag(bipym)-Ag(bipym)}_n repeating units, which consist of the atoms Ag1, Ag2, N1–N4, C1–C8 (unit I) and Ag1A, Ag2, N5–N8,



Figure 4. ORTEP diagram (50% probability level) of a part of the 1D polymer formed by **6**. The alignment of the nitrate anions and the water molecule towards the 1D polymer is presented for one representative case, <) is the interplanar angle of the calculated mean planes of adjacent bipym ligands. All hydrogen atoms, except for the O-bonded ones, have been omitted for clarity. Label "a" refers to atoms of a second asymmetric unit. Selected distances (Å) and angles (°): Ag1–N1 2.357(4), Ag1–N2 2.284(4), Ag2–N3 2.243(3), Ag2–N4 2.397(4), Ag2–N5 2.257(4), Ag2–N6 2.396(5), Ag1–N7a 2.297(4), Ag1–N8a 2.346(4), C5–C4 1.501(6); N3–Ag2–N5 145.04(14), N3–Ag2–N6 137.46(14), N5–Ag2–N6 72.95(14), N3–Ag2–N4 71.95(12), N5–Ag2–N4 130.92(13), N6–Ag2–N4 96.24(12), N2–Ag1–N7a 128.94(13), N2–Ag1–N8a 145.68(14), N7a–Ag1–N8a 71.66(15), N2–Ag1–N1 71.74(13).



Figure 5. Graphical representation of 2D layers formed from 1D chains of **6** in the crystal structure induced by π - π interactions between adjacent 1D polymers (left), together with details of the interaction; <) gives the interplanar angle, and *d* gives the centroid–centroid distance of interacting bipym ligands (right). Labels "a–e" refer to the first to the fifth symmetry-generated asymmetric unit of **6**. The nitrate anions, the water molecules, and all hydrogen atoms are omitted for clarity.

Table 3. Intermolecular hydrogen bond lengths (Å) and angels (°) within the molecular structure of $6.^{\rm [a]}$

D–H	А	D····A	D–H···A
07–H7A	O6	2.860(7)	161.3(6)
O7–H7A	O1	3.308(3)	153.0(3)
O7–H7B	O3	3.346(9)	148.6(5)

[a] D = donor, A = acceptor.

C9–C16 (unit II), are planar (mean plans; unit I: r.m.s.d. = 0.087 Å, unit II: r.m.s.d. = 0.059 Å). However, the 1D chain is not planar, as is shown by the dihedral angles of the neighboring bipym ligands (Figure 4). The silver atoms in 6 are coordinated either by four N-donor atoms of two bipym building blocks to form an AgN₄ entity (Ag2) or by four N-donor atoms and the weakly bonded oxygen atom of one nitrate anion to create an AgN₄O subunit (Ag1). The coordination geometry of the silver atom in the AgN₄ assembly can best be described as strong tetrahedrally distorted and with small N-Ag-N angles induced by the "biting" of the bipym ligands [N5-Ag2-N6 73.0(2) and N3-Ag2-N4 72.0(1)°]; the remaining angles range from 96.2(1) (N6-Ag2-N4) to 145.0(2)° (N3-Ag2-N5). The coordination geometry around the silver atom of the AgN₄O moieties can best be described as distorted square pyramidal with O6 at the apex of the basal AgN₄ plane. The τ parameter of 0.22^[14] affirms the description of the coordination geometry; however, the interaction of the nitrate anion towards Ag1 should not be overstressed. By neglecting the nitrate anion, the coordination geometry around Ag1 closely resembles that of Ag2 (Figure 4).

As described above, the 1D coordination polymers of **6** interact with each other by means of π - π interactions between the bipym units to lead to 2D layers. A representative part of one 2D layer with geometrical details is illustrated in Figure 5.

Complex 8 crystallizes in the monoclinic space group $P2_1/n$ in the form of centrosymmetric homodimetallic $[Ag_2-(bipym)(O_2CCO_2H)_2]$ entities, with a crystallographic imposed inversion center in the middle of the C1–C1a bond. The molecular structure is shown in Figure 6, and the crystallographic data are summarized in Table 5. For complex 8, the formation of a 3D network is observed in the solid state. The {(HO_2CCO_2)Ag(bipym)Ag(O_2CCO_2H)} building blocks interact with each other, which results in the formation of 2D layers based on intermolecular hydrogen bridges. These layers are connected to the 3D network by $\pi-\pi$ interactions between bipym ligands.

The bipym units in **8** act as flexidentate ligands as already observed for **5** and **6** (vide supra). However, as the oxalate dianions become protonated during the formation of **5** (vide supra) and as the anion $[O_2CCO_2H]$ -acts as a monodenate ligand, the silver(I) ions set up AgN₂O arrays. The bond angles of the AgN₂O units range from 70.27(6) (N1-Ag1-N2A) to 154.60(6)° (O1-Ag1-N2), and the r.m.s.d. from planarity of the calculated mean plane of atoms O1, Ag1, N1A, and N2 is 0.157 Å. Thus, the coordination geometry at silver can best be described as trigonal planar. Molecules of **8** are superimposed on each other in the solid state through π - π interactions between the bipym moieties (Figure 7). As shown in Figure 7, the oxygen atom O1 of symmetry-generated equivalents of **8** comes closer to

Figure 6. ORTEP diagram (50% probability level) of homodimetallic **8** in the solid state. All hydrogen atoms, except for the Obonded hydrogen atoms, are omitted for clarity. Selected distances (Å) and angles (°): Ag1–O1 2.237(15), Ag1–N1a 2.4120(17), Ag1–N2 2.3039(17), C1–C1a 1.492(4), C5–C6 1.545(3); O1–Ag1–N2 154.60(6), O1–Ag1–N1a 130.4834(12), N2–Ag1–N1a 70.27(6), C5–O1–Ag1 108.34(12), C1–N2–Ag1 118.99(13), C4–N2–Ag1 124.44(13), C1–N1–Ag1a 115.85(13), C2–N1–Ag1a 127.05(14).

the Ag1 ions. The interatomic distance is 2.980(6) Å, which is significantly shorter than the sum of the van der Waals radii (3.24 Å) of Ag and $O^{[13]}$ The Ag–O contacts in the same range are usually considered as nonbonding.^[15]

Figure 7. Graphical representation of three superimposed molecules of **8** involved in π - π interactions; <) gives the interplanar angle, and *d* the centroid–centroid distance of interacting bipym ligands. Labels "a–e" refer to the first to the fifth symmetry-generated asymmetric unit of **8**. All hydrogen atoms, except for the Obonded hydrogen atoms, have been omitted for clarity.

Because of the carboxylic acid functionalities in **8**, the formation of intermolecular hydrogen bonds is observed in the solid state, which gives rise to the formation of 2D layers (Figure 8). The combination of π - π interactions (Figure 7) and the discussed intermolecular hydrogen bonds results in the formation of a 3D network.

Other Lewis bases that can be added to polymeric [Ag-O₂CCO₂Ag]_n (**3a**) are phosphanes, which may allow the obtainment of lower-aggregated metal-organic species. Thus, **3a-3g** were treated with PR₃ (**9a**, R = *n*Bu; **9b**, R = Ph) in the ratios of 1:2, 1:4 or 1:6, respectively, in dichloromethane or diethyl ether suspensions. After appropriate workup, the coordination compounds [(R₃P)_mAgXAg(PR₃)_m] [R = Ph, X = C₄O₄, m = 1 (**10a**), m = 2 (**10b**); R = *n*Bu, X = O₂CCH₂CO₂, m = 1 (**10c**), m = 2 (**10d**); X = O₂C(CH₂)₂-

Figure 8. Graphical representation of a part of a plane induced by intermolecular hydrogen bonds in the crystal structure of **8**. Lables "a–m" refer to the first to the twelfth symmetry-generated asymmetric unit of **8**. All hydrogen atoms, except for the O-bonded atoms, have been omitted for clarity. Hydrogen interactions: do-nor–H = O4–H1, acceptor = O1, D···A = 2.6017, D–H···A = 1.71. Non-hydrogen intermolecular contact: atom I = Ag1, atom J = O1, d(I-J) = 2.979.

CO₂, m = 1 (10e), m = 2 (10f), m = 3 (10g); X = cis-O₂CCH=CHCO₂, m = 1 (10h), m = 2 (10i), m = 3 (10j); X = trans-O₂CCH=CHCO₂, m = 1 (10k), m = 2 (10l), m = 3(10m); X = para-O₂CC₆H₄CO₂, m = 2 (10n)] could be isolated as colorless to off-white liquids or solids in excellent yields (see Reaction (3), Table 4, and the Experimental Section). Complexes with m = 2 and 3 are more stable than those assemblies with m = 1. While 3a-3g are practically insoluble in common organic solvents (vide supra), the phosphane silver complexes 10a-10n dissolve in most common nonpolar organic solvents.

[Ag ₂ X]	+	$2m PR_3$	>	$[(R_3P)_m\mathbf{Ag}-\mathbf{X}-\mathbf{Ag}(PR_3)_m]$	(3)
3b—3g		9		10a—10n	
		9a, R = Ph 9b, R = <i>n</i> -Bu			

The formation of **10a–10n** was evidenced by elemental analysis and IR, ¹H, ¹³C{¹H}, and ³¹P{¹H} NMR spectroscopy. Additionally, from selected samples, thermogravimetric and differential scanning calorimetric measurements were carried out. In the IR spectra of **10a–10n**, strong \tilde{v}_{CO} vibrations from 1340 to 1586 cm⁻¹ are found, as expected for the dicarboxylate and squarate connectivities (Experimental Section).^[1c,7a,7d,7e]

In the ¹H NMR spectra of **10a–10n**, characteristic resonance signals and coupling patterns are observed for the phosphane ligands and the bridging units X (Experimental Section).^[1b,7] The ³¹P{¹H} NMR spectra of **10a–10n** are

Table 4. Synthesis of homodimetallic complexes 10a-10n.

Compound	X	R	т	Yield (%) ^[a]
10a	C ₄ O ₄	Ph	2	97
10b	C_4O_4	Ph	3	97
10c	$O_2CCH_2CO_2$	<i>n</i> Bu	2	86
10d	$O_2CCH_2CO_2$	<i>n</i> Bu	3	88
10e	$O_2C(CH_2)_2CO_2$	<i>n</i> Bu	1	93
10f	$O_2C(CH_2)_2CO_2$	<i>n</i> Bu	2	83
10g	$O_2C(CH_2)_2CO_2$	<i>n</i> Bu	3	87
10h	cis-O ₂ CCH=CHCO ₂	<i>n</i> Bu	1	93
10i	cis-O ₂ CCH=CHCO ₂	<i>n</i> Bu	2	89
10j	cis-O ₂ CCH=CHCO ₂	<i>n</i> Bu	3	95
10k	trans-O ₂ CCH=CHCO ₂	<i>n</i> Bu	1	93
10l	trans-O ₂ CCH=CHCO ₂	<i>n</i> Bu	2	95
10m	trans-O ₂ CCH=CHCO ₂	<i>n</i> Bu	3	92
10n	para-O ₂ CC ₆ H ₄ CO ₂	<i>n</i> Bu	2	96

[a] Based on 3a-3g.

very informative. Relative to free phosphanes PR₃ (9a, -32.3 ppm; 9b, -6.0 ppm),^[16] the signals for the coordinated phosphanes in the metal–organic compounds 10a–10n appear at a lower field (Experimental Section). In general, the resonance signals are broad, which indicate thermal-dependent exchange processes on the NMR time scale as discussed elsewhere.^[17] However, this intermolecular ligand exchange process becomes fast on the NMR time scale for 10k and 10l. For 10k two doublets at -0.2 ppm [672 Hz ($J_{107Ag31P}$), 773 Hz ($J_{109Ag31P}$)] and for 10l one broad singlet at -7.4 ppm are found, because of the presence of ¹⁰⁷Ag and ¹⁰⁹Ag isotopes [relative natural abundance of ¹⁰⁷Ag 51.83% and ¹⁰⁹Ag 48.17%].^[18]

The thermal decomposition of selected coordination complexes was studied by thermogravimetry (TG) and differential scanning calorimetry (DSC) to determine their suitability for spin-coating processing (vide infra). As an example, the TG trace for 10f is shown in Figure 9. Experiments were conducted at atmospheric pressure under a nitrogen atmosphere. For most of the complexes, their thermal degradation starts at 47 °C and is completed above 357 °C (Experimental Section). The weight losses are accompanied by residues in the TG pan, the amount of which is comparable to the theoretical percentage of metallic silver present in the complex, although small amounts (0.2–2.1%, except for 10k and 10m) of additional material are also formed. Evidently, these complexes eliminate the ancillary ligands L (vide supra) upon heating without significant volatilization of the intact disilver-dicarboxylates and -squarates, respectively. Thus, at atmospheric pressure, the majority of the studied disilver species 10a-10n are nonvolatile complexes, and hence, are best suited for spin-coating depositions; however, one exception is 10d, which qualifies as a CVD precursor (see below) as can be shown by temperature-programmed mass spectrometry.^[8] The DSC traces are characterized by at least two overlapping endothermic and exothermic isotherms (Experimental Section).

Silver films were deposited on glass substrates from **10d** by using a vertical CVD reactor with a direct liquid injection system. The precursor was dissolved in ethanol, and the solution was injected through a nozzle in the evapora-

Figure 9. TG trace of **10f** (heating rate 8 Kmin^{-1} , nitrogen atmosphere, $20 \text{ dm}^3 \text{ h}^{-1}$).

tion chamber. The deposition took place at temperatures 250–350 °C. Silver films with a thickness of 200–300 nm could be obtained. According to XRD studies, silver was obtained in the cubic modification (Figure 10). EDX measurements show a carbon content of 30%. SEM images show uneven films with a connected-island-like structure (Figure 11).

Figure 10. XRD spectra of the silver film formed by **10d** (300 °C deposition temperature, bottom), and the calculated XRD spectra of cubic silver (top).

30 µm

3 µm

Figure 11. SEM images of the 240-nm-thick silver film formed by using **10d** as the precursor at deposition temperature of 300 °C.

Complexes **10e** and **10f** were subjected to spin-coating deposition experiments. For complex **10e** conductive silver films could be obtained with a film resistivity of $3.4 \ \mu\Omega$ cm. The film thickness (mean value of about 2.5 μ m, determined by profilometer) was not homogeneous because of the solvent used acetonitrile, i.e. in the wafer center the thickness of the film was 3.2 μ m. This effect can additionally be caused by a non-Newtonian sample flow. Adhesion of the film was very good for the thin film segments. The films were investigated by SEM studies (Figure 12). EDX

Figure 12. SEM images of the silver deposition obtained from **10e** (top) and **10f** (bottom) as precursor materials.

Figure 13. EDX diagram of the silver deposition obtained from **10e** (top) and **10f** (bottom) as precursors.

analysis shows that, in addition, carbon and oxygen impurities are present; the peak for oxygen is most probably attributed to the wafer material (glass, oxidized silicon) because the films obtained are not completely dense (Figure 13). The elimination of pores by optimizing the sample preparation and the thermolysis conditions is important in order to reduce the film resistivity.

Conclusions

A straightforward synthetic methodology for the preparation of disilver-dicarboxylates and -squarates of type $[Ag_2X]$ (X = oxalate, squarate, malonate, succinate, maleicate, fumarate, and terephthalate), coordination polymers $[(bipym)Ag(O_2CCO_2)]_n$, $[(bipym)(Ag(O_2CCO_2H))_2]_n$ (bipym = bipyrimidine), and coordination complexes $[(R_3P)_m$ - $AgXAg(PR_3)_m$ (R = Ph, nBu) is discussed. The use of $[(nBu_3P)_3AgO_2CCH_2CO_2Ag(PnBu_3)_3]$ as CVD and [(nBu₃P)AgO₂C(CH₂)₂CO₂Ag(PnBu₃)] as well as [(nBu₃P)₂- $AgO_2C(CH_2)_2CO_2Ag(PnBu_3)_2$] as spin-coating precursors for the preparation of nanocrystalline silver films on glass or pieces of TiN-coated oxidized silicon wafer materials is possible. Conductive silver films with a thickness of 200-300 nm could be deposited from $[(nBu_3P)_2AgO_2CCH_2 CO_2Ag(PnBu_3)_2$ on glass by using a vertical cold-wall CVD reactor. For spin-coating, complexes [(nBu₃P)AgO₂- $C(CH_2)_2$ -

 $CO_2AgP(nBu_3)$] and $[(nBu_3P)_2AgO_2C(CH_2)_2CO_2AgP(nBu_3)_2]$ were applied. Heating of the deposited silver materials at a heating rate of 15 K min⁻¹ to 450 °C gave silver layers on TiN-coated oxidized silicon substrates. The EDX analyses monitored silver films, which are contaminated with traces of oxygen and carbon.

Experimental Section

General: All reactions were carried out under an atmosphere of nitrogen by using standard Schlenk techniques. Tetrahydrofuran, diethyl ether, and *n*-hexane were purified by distillation from so-dium/benzophenone ketyl; dichloromethane was purified by distillation from calcium hydride. Celite (purified and annealed, Erg. B.6, Riedel de Haen) was used for filtrations.

Instruments: Infrared spectra were recorded with a Perkin-Elmer FTIR spectrometer Spectrum 1000. ¹H NMR spectra were recorded with a Bruker Avance 250 spectrometer operating at 250.130 MHz in the Fourier transform mode; ¹³C{¹H} NMR spectra were recorded at 62.860 MHz. Chemical shifts are reported in δ units (parts per million) downfield from tetramethylsilane with the solvent as the reference signal [¹H NMR: CDCl₃ (99.8%), $\delta =$ 7.26; (CD₃)₂CO (99.9%), $\delta = 2.05$; CD₃CN (99.8%), $\delta = 1.94$. ¹³C{¹H} NMR: CDCl₃ (99.8%), δ = 77.16; (CD₃)₂CO (99.9%), δ = 29.84, 206.26]. ${}^{31}P{}^{1}H$ NMR spectra were recorded at 101.255 MHz in CDCl₃ with P(OMe)₃ as external standard [δ = 139.0, relative to H₃PO₄ (85%) with $\delta = 0.00$]. Thermogravimetric studies were carried out with a Perkin-Elmer System Pyris TGA 6 instrument with a constant heating rate of 8 Kmin^{-1} under N₂ (20.0 dm³ h⁻¹). DSC experiments were carried out with a Perkin-Elmer System Pyris DSC 6 instrument with a constant heating rate of 8 K min⁻¹ under N₂ (20.0 dm³ h⁻¹). Melting points were determined using analytically pure samples sealed off in nitrogen purged capillaries, on a Gallenkamp MFB 595 010 M melting point apparatus. Microanalyses were performed with a C, H, N analyzer FlashAE 1112 instrument (Thermo Company).

The CVD experiments were performed in a vertical cold-wall reactor with a stagnation-point-flow geometry. The precursor was dissolved in tetrahydrofuran and introduced to the reactor by using a pulsed spray evaporation technique that allows a control of the feeding rate between 0.5 and 20 mL min⁻¹. The precursor solution was mixed in a preheated flow of nitrogen in the heated evaporation chamber. The inlet tube, with an inner diameter of 10 mm, was maintained at a temperature slightly above the evaporation temperature to prevent condensation. The glass substrates were cleaned with hot sulfuric acid, acetone, and ethanol in an ultrasonic bath and placed on a resistively heated ceramic block. The temperature was measured with a thermocouple located directly at the substrate. A rotary oil pump equipped with a cooling trap was used to keep the reactor system at a pressure of 1 mbar during the deposition process. The precursor solutions were prepared with tetrahydrofuran with analytical quality, and the nitrogen carrier gas was dried by using standard methods before use. Evaporation temperature = 425 K, deposition temperature = 525-675 K, deposition time = 30-50 min, and pressure = 1 mbar. The flow rate of the carrier gas nitrogen was 40 sccm, and the concentration of the precursor solution in tetrahydrofuran was between 1.2 g L^{-1} and 3 gL^{-1} . The thickness of the films was estimated gravimetrically by assuming that the deposit has the density of bulk silver. The films were inspected by using optical microscopy (Leica DM LM, magnification 1500) and analyzed with X-ray diffraction (XRD) (X'pert pro MRD, Phillips) and scanning electron microscopy (SEM) (Hitachi S-450). The electrical resistivity was measured by using a home-built four-point probe setup.

The spin-coating experiments were carried out on an industrial spin-coating system (Suss Microtec Inc.) with a closed deposition chamber. A precursor sample of 1.6 g of the complex was diluted in 0.4 mL tetrahydrofuran and mixed for 2 min under a nitrogen stream. Since tetrahydrofuran is highly volatile, a slow rotation speed of 800 rpm was chosen. The sample was dispensed on the precleaned TiN-coated Si-wafer, and after spin-off for 10 s, the film was almost dry. The applied sintering parameters were: heating rate 15 K min⁻¹, maximum sintering temperature 450 °C, and dwell time 0.5 h. The film resistivity was determined by using a four-point resistance instrument from Omnimap company.

Reagents: Bipyrimidine^[19] and [(bipym)AgNO₃]^[20] were prepared according to published procedures. Complexes 3a-3g were synthesized by the preparation protocol given in the literature.^[1b] All other chemicals were purchased by commercial suppliers and were used without further purification.

[(bipym)AgO₂CCO₂Ag]_n (5) and [HO₂CCO₂Ag(bipym)AgO₂-CCO₂H] (8): Compound 5 was synthesized by mixing a hot water solution (30 mL) containing 6 (472 mg, 0.72 mmol) with 7 (210 mg, 0.36 mmol) dissolved in water (20 mL). After stirring the reaction mixture for 1 h at 25 °C, complex 5 precipitated as a colorless to pale yellow solid, which is poorly soluble in water and insoluble in common organic solvents including tetrahydrofuran, dimethylsulf-oxide, and dichloromethane. Complex 8 was separated as a by-product in the course of washing the precipitate with water (3 × 30 mL, 70 °C). Yield: 5, 169 mg (0.34 mmol, 47% based on 6); 8, 4 mg (0.01 mmol, 1.4% based on 6). Complex 5: $C_{10}H_6Ag_2N_4O_4$ ·H₂O (497.946): C 24.12, H 2.02, N 11.25; found C 24.45, H 1.90, N 11.37. IR (KBr): $\tilde{v} = 1312$, 1406, 1560, 1596, 1602, 1608 (s, C=C) (s, N=C) (s, C–O), 3368 (s, OH) cm⁻¹. Complex 8:

IR (KBr): $\tilde{v} = 1405$, 1560, 1627, 1701 (s, C=C) (s, N=C) (s, C-O), 3044, 3064, 3448 (OH) cm⁻¹.

[(Ph₃P)₂AgC₄O₄Ag(PPh₃)₂] (10a): Complex 10a was prepared by addition of 9a (2.18 g, 8.31 mmol) to a suspension of 3a (0.68 g, 2.08 mmol) in dichloromethane (30 mL) at 0 °C. After stirring for 2 h at this temperature, all volatile materials were removed by an oil-pump vacuum. A colorless solid remained. Yield: 2.8 g (2.0 mmol, 97% based on 3a). Mp: 169 °C (decomposition). C₂₈H₂₀Ag₂O₄P₄ (1376.86): C 24.42, H 1.46; found C 24.81, H 1.73%. IR (KBr): $\tilde{v} = 1507$ (s, C–O), 1560 (s, C–O) cm⁻¹. ¹H NMR (250 MHz, CDCl₃, 25 °C): $\delta = 7.29-7.36$ (m, 60 H, Ph) ppm. ¹³C{¹H} NMR (62.9 MHz, CDCl₃, 25 °C): $\delta = 128.9$ (d, *J*_{CP} = 7 Hz, ^mC/Ph), 129.3 (°C/Ph) ppm; notice that the CO carbon atoms could not be detected under the measurement conditions applied. ³¹P{¹H} NMR (101.3 MHz, CDCl₃, 25 °C): $\delta = -3.7$ ppm.

[(Ph₃P)₃AgC₄O₄Ag(PPh₃)₃] (10b): The metal–organic compound **10b** was prepared by the same reaction protocol as described for **10a**: phosphane **9a** (3.13 g, 11.93 mmol), disilver squarate **3a** (0.65 g, 1.99 mmol). After appropriate workup, complex **10b** was isolated as a colorless solid. Yield: 3.7 g (1.90 mmol, 97% based on **3a**). Mp: 128 °C. C₄₀H₃₀Ag₂O₄P₆ (1900.54): C 25.28, H 1.59; found C 25.37, H 1.88%. IR (KBr): $\tilde{v} = 1340$ (m, C–O), 1582 (s, C–O) cm⁻¹. ¹H NMR (250 MHz, CDCl₃, 25 °C): $\delta = 7.29-7.34$ (m, 90 H, Ph) ppm. ¹³C{¹H} NMR (62.9 MHz, CDCl₃, 25 °C): $\delta = 128.0$ (d, $J_{CP} = 8$ Hz, ^mC/Ph), 129.6 (°C/Ph), 134.2 (d, $J_{CP} = 18$ Hz, ^{*i*}C) ppm; note that the CO carbon atoms could be not detected under the used conditions. ³¹P{¹H} NMR (101.3 MHz, CDCl₃, 25 °C): $\delta = -2.3$ ppm.

[(nBu₃P)₂AgO₂CCH₂CO₂Ag(PnBu₃)₂] (10c): Complex 10c could be synthesized by reacting 9b (2.42 g, 12.0 mmol) with 3c (0.95 g, 3.0 mmol) in tetrahydrofuran (30 mL) at 25 °C. The solution was stirred for 2 h and afterwards filtered through a pad of Celite. All volatile materials were removed by an oil-pump vacuum, whereby 10c was obtained as a pale brown oil. Yield: 2.92 g (2.59 mmol, 86% based on 3c). $C_{51}H_{110}O_4Ag_2P_4$ (1127.06): C 54.35, H 9.84; found C 54.77, H 9.82%. IR (NaCl): v = 1417 (s, C-O), 1558 (vs, C–O) cm⁻¹. ¹H NMR (250 MHz, CDCl₃, 25 °C): $\delta = 0.87$ [t, ³J_{HH} = 6.6 Hz, 36 H, P(CH₂)₃CH₃], 1.39–1.58 [m, 72 H, P(CH₂)₃CH₃], 3.16 (s, 2 H, O₂CCH₂CO₂) ppm. ¹³C{¹H} NMR (62.9 MHz, CDCl₃, 25 °C): δ = 13.7 [P(CH₂)₃CH₃], 18.9 (O₂CCH₂CO₂), 24.4 [d, $J_{CP} = 13 \text{ Hz}$, $P(CH_2)_2CH_2CH_3$], 25.1 (d, $J_{CP} = 14 \text{ Hz}$, PCH₂CH₂CH₂CH₃), 27.6 [PCH₂(CH₂)₂CH₃], 174.3 (CO) ppm. ³¹P{¹H} NMR (101.3 MHz, CDCl₃, 25 °C): δ = -6.8 ppm. TGA (8 K/min): $T_{\text{start}} = 100 \text{ °C}$, $T_{\text{end}} = 315 \text{ °C}$, $\Delta m = 79.2\%$. DSC (8 K/ min): peak 1: T = 74 °C, $\Delta H_1 = 1.9$ J/g; peak 2: T = 145 °C, ΔH_2 = -12.6 J/g; peak 3: T = 234 °C, $\Delta H_3 = 11.5$ J/g; peak 4: T =352 °C, $\Delta H_4 = -6.9$ J/g.

[(*n*Bu₃P)₃AgO₂CCH₂CO₂Ag(P*n*Bu₃)₃] (10d): Compound 10d was synthesized in the same manner as 10c. Thus, 9b (3.64 g, 18.0 mmol) was treated with 3c (0.95 g, 3.0 mmol). After appropriate workup, 10d was isolated as a colorless oil. Yield: 4.08 g (2.66 mmol, 88% based on 3c). C₇₅H₁₆₄O₄Ag₂P₆ (1531.70): C 58.81, H 10.79; found C 58.59, H 10.62%. IR (NaCI]): $\tilde{v} = 1416$ (s, C–O), 1552 (vs, C–O) cm⁻¹. ¹H NMR (250 MHz, CDCl₃, 25 °C): $\delta = 0.86$ [t, ³J_{HH} = 6.7 Hz, 54 H, P(CH₂)₃CH₃], 1.34–1.56 [m, 108 H, P(CH₂)₃CH₃], 3.06 (s, 2 H, O₂CCH₂CO₂) ppm. ¹³C{¹H} NMR (62.9 MHz, CDCl₃, 25 °C): $\delta = 13.9$ [P(CH₂)₃CH₃], 19.2 (O₂CCH₂CO₂), 24.6 [d, J_{CP} = 13 Hz, P(CH₂)₂CH₂CH₃], 25.4 (d, J_{CP} = 12 Hz, PCH₂CH₂CH₂CH₃), 27.6 [d, J_{CP} = 5 Hz, PCH₂(CH₂)₂-

CH₃], 173.4 (CO) ppm. ³¹P{¹H} NMR (101.3 MHz, CDCl₃, 25 °C): $\delta = -9.5$. TGA (8 K/min): $T_{\text{start}} = 99$ °C, $T_{\text{end}} = 356$ °C, Δm

= 85.7%. DSC (8 K/min): peak 1: T = 154 °C, $\Delta H_1 = 6.6$ J/g; peak 2: T = 165 °C, $\Delta H_2 = 7.1$ J/g; peak 3: T = 284 °C, $\Delta H_3 = -65.3$ J/g.

[(nBu₃P)AgO₂C(CH₂)₂CO₂Ag(PnBu₃)] (10e): Complex 10e was synthesized by applying the same preparation procedure as discussed for 10a: 9b (0.12 g, 0.58 mmol), 3d (0.097 g, 0.29 mmol). After appropriate workup, 10e was obtained as a yellow oil. Yield: 0.20 g (0.27 mmol, 93% based on 3d). $C_{28}H_{58}Ag_2O_4P_2$ (736.45): C 45.66, H 7.94; found C 45.78, H 7.99%. IR (NaCl): $\tilde{v} = 1380$ (s, C–O), 1553 (vs, C–O) cm⁻¹. ¹H NMR (250 MHz, CDCl₃, 25 °C): $\delta = 0.84$ [t, ${}^{3}J_{\text{HH}} = 7.0$ Hz, 18 H, P(CH₂)₃CH₃], 1.27–1.55 [m, 36] H, $P(CH_2)_3CH_3$, 2.50 [br. s, 4 H, $O_2C(CH_2)_2CO_2$] ppm. ¹³C{¹H} NMR (62.9 MHz, CDCl₃, 25 °C): $\delta = 14.0 [P(CH_2)_3 CH_3]$, 24.7 [d, $J_{\rm CP} = 15 \,\text{Hz}, P(\rm CH_2)_2 CH_2 CH_3], 25.6 \,\text{(d, } J_{\rm CP} = 19 \,\text{Hz},$ PCH₂CH₂CH₂CH₃), 28.2 [PCH₂(CH₂)₂CH₃], 31.3 [O₂C(CH₂)₂-CO₂], 174.7 (CO) ppm. ³¹P{¹H} NMR (101.3 MHz, CDCl₃, 25 °C): δ = -0.4 ppm. TGA (8 K/min): T_{start} = 151 °C, T_{end} = 411 °C, $\Delta m = 69.1$ %. DSC (8 K/min): peak 1: T = 253 °C, $\Delta H_1 =$ 3.5 J/g.

 $[(nBu_3P)_2AgO_2C(CH_2)_2CO_2Ag(PnBu_3)_2]$ (10f): Complex 10f was synthesized by the reaction protocol described for the synthesis of 10c: 9b (2.42 g, 12.0 mmol), 3d (0.99 g, 3.0 mmol). After appropriate workup, 10f was obtained as a pale brown oil. Yield: 2.86 g (2.51 g, 83% based on 3d). C₅₂H₁₁₂Ag₂O₄P₄ (1141.09): C 54.73, H 9.89; found C 54.94, H 9.81%. IR (NaCl): v = 1383 (s, C-O), 1555 (vs, C–O) cm⁻¹. ¹H NMR (250 MHz, CDCl₃, 25 °C): $\delta = 0.63$ [t, ${}^{3}J_{\text{HH}} = 6.8 \text{ Hz}, 36 \text{ H}, P(CH_{2})_{3}CH_{3}], 1.11-1.30 \text{ [m, 72 H, P(CH_{2})_{3}-1.11-1.30]}$ CH₃], 2.28 [s, 4 H, $O_2C(CH_2)_2CO_2$] ppm. ¹³C{¹H} NMR (62.9 MHz, CDCl₃, 25 °C): δ = 13.9 [P(CH₂)₃CH₃], 24.6 [d, J_{CP} = 25.4 (d, *J*_{CP} 12 Hz, $P(CH_2)_2CH_2CH_3],$ = 12 Hz, PCH₂CH₂CH₂CH₃), 25.8 [O₂C(CH₂)₂CO₂], 27.7 [PCH₂(CH₂)₂-CH₃], 179.3 (CO) ppm. ${}^{31}P{}^{1}H$ NMR (101.3 MHz, CDCl₃, 25 °C): δ = -7.9 ppm. TGA (8 K/min): T_{start} = 125 °C, T_{end} = 400 °C, $\Delta m = 80.6$ %. DSC (8 K/min): peak 1: T = 86 °C, $\Delta H_1 =$ 2.6 J/g; peak 2: T = 243 °C, $\Delta H_2 = 15.1 \text{ J/g}$; peak 3: T = 274 °C, $\Delta H_3 = -5.3 \text{ J/g.}$

[(nBu₃P)₃AgO₂C(CH₂)₂CO₂Ag(PnBu₃)₃] (10g): Complex 10g was synthesized as described for 10c; 9b (3.64 g, 18.0 mmol), 3d (0.99 g, 3.0 mmol). After appropriate workup, complex 10g could be isolated as a colorless oil. Yield: 4.06 g (2.62 mmol, 87% based on 3d). C₇₆H₁₆₆O₄Ag₂P₆ (1545.73): C 59.06, H 10.82; found C 59.33, H 11.01%. IR (NaCl): $\tilde{v} = 1376$ (s, C–O), 1561 (vs, C–O) cm⁻¹. ¹H NMR (250 MHz, CDCl₃, 25 °C): $\delta = 0.83$ [t, ³J_{HH} = 6.5 Hz, 54 H, P(CH₂)₃CH₃], 1.33–1.45 [m, 108 H, P(CH₂)₃CH₃], 2.47 [s, 4 H, O₂C(CH₂)₂CO₂] ppm. ¹³C{¹H} NMR (62.9 MHz, CDCl₃, 25 °C): $\delta = 13.6$ [P(CH₂)₃CH₃], 24.3 [d, J_{CP} = 12 Hz, P(CH₂)₂CH₂CH₂CH₃], 23.6 [O₂C(CH₂)₂CO₂], 25.3 (PCH₂CH₂CH₂CH₂CH₃) 27.3 [PCH₂-(CH₂)₂CH₃], 177.3 (CO) ppm. ³¹P{¹H} NMR (101.3 MHz, CDCl₃, 25 °C): $\delta = -14.4$ ppm. TGA (8 K/min): T_{start} = 101 °C, T_{end} = 349 °C, $\Delta m = 83.9\%$. DSC (8 K/min): peak 1: T = 264 °C, $\Delta H_1 = -83.7$ J/g; peak 2: T = 273 °C, $\Delta H_2 = 41.4$ J/g.

[*cis*-(*n*Bu₃P)AgO₂CCH=CHCO₂Ag(P*n*Bu₃)] (10h): For the synthesis of 10h, complex 9b (584 mg, 2.9 mmol, 0.72 mL) was treated with 3e (500 mg, 1.5 mmol) in dichloromethane (30 mL) at 0 °C. The reaction solution was stirred for 2 h at 0 °C and afterwards filtered through a pad of Celite. All volatiles were removed by an oil-pump vacuum, and 10h was obtained as a pale brown oil. Yield: 1.04 g (1.4 mmol, 93% based on 3e). C₂₈H₅₆Ag₂O₄P₂ (734.43): C 45.79, H 7.69; found C 45.34, H 7.52%. IR (NaCl): $\tilde{v} = 1556$ (vs, C–O), 1638 (m, C=C) cm⁻¹. ¹H NMR (250 MHz, CDCl₃, 25 °C): $\delta = 0.85$ [t, ³J_{HH} = 7.0 Hz, 18 H, P(CH₂)₃CH₃], 1.37–1.58 [m, 36 H, P(CH₂)₃CH₃], 6.06 [s, 2 H, O₂C(CH)₂CO₂] ppm. ¹³C{¹H} NMR (62.9 MHz, CDCl₃, 25 °C): $\delta = 14.0$ [P(CH₂)₃CH₃], 24.6 [d, J_{CP} =

14 Hz, P(CH₂)₂CH₂CH₃], 25.3 (d, $J_{CP} = 20$ Hz, PCH₂CH₂CH₂CH₃), 28.0 [d, $J_{CP} = 3$ Hz, PCH₂(CH₂)CH₃], 130.7 [O₂C(CH)₂CO₂], 175.3 (CO) ppm. ³¹P{¹H} NMR (101.3 MHz, CDCl₃, 25 °C): $\delta = -2.3$ (d, ¹ $J_{109/107Ag31P} = 677$ Hz) ppm.

[*cis*-(*n*Bu₃P)₂AgO₂CCH=CHCO₂Ag(P*n*Bu₃)₂] (10i): Complex 10i was prepared in the same manner as 10h by reacting 9b (127 mg, 6.3 mmol, 1.57 mL) with 3e (500 mg, 1.6 mmol) at 0 °C. Yield: 1.58 g (1.4 mmol, 89% based on 3e). $C_{52}H_{108}Ag_2O_4P_4$ (1139.06): C 54.83, H 9.73; found C 55.09, H 7.64%. IR (NaCl): $\tilde{v} = 1208$ (s, C–O), 1580 (vs, C–O) cm⁻¹. ¹H NMR (250 MHz, CDCl₃, 25 °C): $\delta = 0.87$ [t, ³*J*_{HH} = 5.6 Hz, 36 H, P(CH₂)₃CH₃], 1.43–1.66 [m, 72 H, P(CH₂)₃CH₃], 6.07 [s, 2 H, O₂C(CH)₂CO₂] ppm. ¹³C{¹H} NMR (62.9 MHz, CDCl₃, 25 °C): $\delta = 13.9$ [P(CH₂)₃CH₃], 24.6 [d, *J*_{CP} = 13 Hz, P(CH₂)₂CH₂CH₃], 25.3 (d, *J*_{CP} = 14 Hz, PCH₂CH₂-CH₂CH₃), 28.0 [d, *J*_{CP} = 3 Hz, PCH₂(CH₂)₂CH₃], 130.5 [O₂C(CH)₂-

CO₂], 175.0 (CO) ppm. ³¹P{¹H} NMR (101.3 MHz, CDCl₃, 25 °C): $\delta = -5.3$ ppm.

[*cis*-(*n*Bu₃P)₃AgO₂CCH=CHCO₂Ag(P*n*Bu₃)₃] (10j): Complex 10j was prepared as discussed for 10h: 9b (368 mg, 1.82 mmol, 0.45 mL), 3e (100 mg, 0.30 mmol). Yield: 445 mg (0.29 mmol, 95% based on 3e). C₇₆H₁₆₄Ag₂O₄P₆ (1543.69): C 59.13, H 10.71; found C 58.87, H 10.83%. IR (NaCl): $\tilde{v} = 1463$ (m, C–O), 1564 (m, C–O), 1685 (w, C=C) cm⁻¹. ¹H NMR (250 MHz, CDCl₃, 25 °C): $\delta = 0.78$ [t, ³*J*_{HH} = 7.5 Hz, 54 H, P(CH₂)₃CH₃], 1.22–1.51 [m, 108 H, P(CH₂)₃CH₃], 6.10 (s, 2 H, CH) ppm. ¹³C{¹H} NMR (62.9 MHz, CDCl₃, 25 °C): $\delta = 13.8$ [P(CH₂)₃CH₃], 24.5 [d, *J*_{CP} = 13 Hz, P(CH₂)₂CH₂CH₃], 25.3 (d, *J*_{CP} = 11 Hz, PCH₂CH₂CH₂CH₂CH₃), 27.6 [d, *J*_{CP} = 5 Hz, PCH₂(CH₂)₂CH₃], 135.9 [O₂C(CH)₂CO₂], 169.0 (CO) ppm. ³¹P{¹H} NMR (101.3 MHz, CDCl₃, 25 °C): $\delta = -9.5$ ppm.

[trans-(nBu₃P)AgO₂CCH=CHCO₂Ag(PnBu₃)] (10k): To a suspension of 3f (0.14 g, 0.41 mmol) in dichloromethane (20 mL) was added 9b (0.16 g, 0.2 mL, 0.81 mmol) in a single portion. At the time the reaction mixture became clear, stirring was continued for 1 h and then the reaction mixture was filtered through a pad of Celite. Afterwards, all volatiles were removed by an oil-pump vacuum, and 10k was obtained as a yellow oil. Yield: 0.28 g (0.38 mmol, 93% based on 3f). $C_{28}H_{56}Ag_2O_4P_2$ (734.48): C 45.78, H 7.69; found C 45.98, H 7.81%. IR (NaCl): $\tilde{v} = 1360$ (m, C–O), 1568 (m, C-O), 1695 (w, C=C) cm⁻¹. ¹H NMR (250 MHz, CDCl₃, 25 °C): δ = 0.84 (t, ³J_{HH} = 7.0 Hz, 18 H, CH₃), 1.27–1.55 (m, 36 H, CH₂), 6.83 (d, ${}^{3}J_{HH}$ = 1 Hz, 2 H, CH) ppm. ${}^{13}C{}^{1}H$ NMR (62.9 MHz, CDCl₃, 25 °C): δ = 14.1 [P(CH₂)₂CH₃], 24.7 [d, J_{CP} = 12 Hz, $P(CH_2)_2CH_2CH_3$], 25.6 (d, $J_{CP} = 12$ Hz, PCH_2CH_2 -CH₂CH₃), 27.9 [PCH₂(CH₂)₂CH₃], 135.6 (CH), 174.7 (CO) ppm. ³¹P{¹H} NMR (101.3 MHz, CDCl₃, 25 °C): $\delta = -0.2$ (d, $J_{107Ag31P}$ = 672 Hz), -0.2 (d, J_{109Ag31P} = 773 Hz) ppm. TGA (8 K/min): T_{start} = 112 °C, T_{end} = 358 °C, Δm = 80.3 %. DSC (8 K/min): peak: T = 264 °C, $\Delta H = 46.5$ J/g.

[*trans*-(*n*Bu₃P)₂AgO₂CCH=CHCO₂Ag(P*n*Bu₃)₂] (10l): The synthesis of 10l was performed as discussed for the preparation of 10k. Thus 3f (137 mg, 0.42 mmol) was treated with 9b (329 mg, 0.40 mL, 1.66 mmol). Complex 10l was obtained as a colorless oil. Yield: 460 mg (0.4 mmol, 95% based on 3f). C₅₂H₁₁₀Ag₂O₄P₄ (1139.07): C 54.83, H 9.73; found C 54.17, H 9.50%. IR (NaCl): $\tilde{v} = 1377$ (s, C–O), 1586 (s, C–O), 1705 (m, C=C) cm⁻¹. ¹H NMR (250 MHz, CDCl₃, 25 °C): $\delta = 0.88$ [t, ³J_{HH} = 7.0 Hz, 36 H, P(CH₂)₃CH₃], 1.41–1.57 [m, 72 H, P(CH₂)₃CH₃], 6.71 (s, 2 H, CH) ppm. ¹³C {¹H} NMR (62.9 MHz, CDCl₃, 25 °C): $\delta = 14.1$ [P(CH₂)₃CH₃], 24.8 [P(CH₂)₂CH₂CH₃], 25.6 (PCH₂CH₂CH₂CH₃), 27.9 [PCH₂(CH₂)₂-CH₃], 135.9 (CH), 173.4 (CO) ppm. ³¹P{¹H} NMR (101.3 MHz,

CDCl₃, 25 °C): δ = -7.4 ppm. TGA (8 K/min): T_{start} = 74 °C, T_{end} = 330 °C, Δm = 67.4%. DSC (8 K/min): peak: T = 216 °C, ΔH = 22.2 J/g.

[*trans*-(*n*Bu₃P)₃AgO₂CCH=CHCO₂Ag(P*n*Bu₃)₃] (10m): Complex 10m was synthesized as described for 10k: 3f (126 mg, 0.38 mmol), 9b (454 mg, 0.55 mL, 2.29 mmol). After appropriate workup, 10m could be isolated as a colorless oil. Yield: 540 mg (3.5 mmol, 92% based on 3f). C₇₆H₁₆₄Ag₂O₄P₆ (1543.71): C 59.13, H 10.71; found C 59.29, H 10.95%. IR (NaCl): $\tilde{v} = 1377$ (m, C–O), 1567 (m, C–O), 1706 (s, C=C) cm⁻¹. ¹H NMR (250 MHz, CDCl₃, 25 °C): $\delta = 0.90$ [t, ³J_{HH} = 7.0 Hz, 54 H, P(CH₂)₃CH₃], 1.42–1.55 [m, 108 H, P(CH₂)₃CH₃], 6.69 (s, 2 H, CH) ppm. ¹³C{¹H} NMR (62.9 MHz, CDCl₃, 25 °C): $\delta = 14.0$ [P(CH₂)₃CH₃], 24.6 [d, J_{CP} = 15 Hz, P(CH₂)₂CH₂CH₃], 25.5 (d, J_{CP} = 10 Hz, PCH₂CH₂CH₂CH₂CH₃), 27.7 [d, J_{CP} = 6 Hz, PCH₂(CH₂)₂CH₃], 134.3 (CH), 173.9 (CO) ppm. ³¹P{¹H} NMR (101.3 MHz, CDCl₃, 25 °C): $\delta = -12.2$ ppm. TGA (8 K/min): $T_{\text{start}} = 100$ °C, $T_{\text{end}} = 484$ °C, $\Delta m = 79.7\%$. DSC (8 K/min): peak: T = 311 °C, $\Delta H = -34.3$ J/g.

[(*n***Bu₃P)₂AgO₂C-1-C₆H₄-4-CO₂Ag(***n***-PBu₃)₂] (10n): Complex 10n was synthesized by addition of 9b (610 mg, 0.74 mL, 3.0 mmol) to a suspension of 3g (300 mg, 0.8 mmol) in diethyl ether (40 mL) at 25 °C. After stirring for 2 h, the reaction mixture was filtered through a pad of Celite, and all volatiles were removed by an oilpump vacuum. A yellow hygroscopic solid remained. Yield: 860 mg (0.7 mmol, 96%, based on 3g). Mp: 27 °C. C₅₆H₁₁₂Ag₂O₄P₄ (1189.14): C 56.56, H 9.49; found 56.39, H 946. IR (KBr): \tilde{v} = 1370 (s, C–O), 1565 (s, C–O), 1931 (w, C=C) cm⁻¹. ¹H NMR (250.1 MHz, CDCl₃, 25 °C): \delta = 0.79 [t, ³***J***_{HH} = 6.9 Hz, 36 H, P(CH₂)₃CH₃], 1.28–1.65 [m, 72 H, P(CH₂)₃CH₃], 7.93 (s, 4 H, Ph) ppm. ¹³C{¹H} NMR (62.9 MHz, CDCl₃, 25 °C): \delta = 13.3 [P(CH₂)₃-**

CH₃], 24.1 [d, $J_{CP} = 11$ Hz, P(CH₂)₂CH₂CH₃], 25.0 (d, $J_{CP} = 12$ Hz, PCH₂CH₂CH₂CH₃), 27.2 [PCH₂(CH₂)₂CH₃], 128.2 (CH), 139.0 (^{*i*}C), 172.3 (CO) ppm. ³¹P{¹H} NMR (101.3 MHz, CDCl₃, 25 °C): $\delta = -8.4$ ppm. ³¹P{¹H} NMR (101.3 MHz, CDCl₃, -60 °C):

Table 5. Crystal and intensity collection data for 5, 6, and 8.

	5	6	8
Formula	C ₅ H ₇ Ag ₁ N ₂ O ₄	C ₁₀ H ₁₄ Ag ₂ N ₄ O ₈	C ₆ H ₄ AgN ₂ O ₄
Fw	267.00	674.11	275.98
Crystal system	triclinic	orthorhombic	monoclinic
Space group	$P\overline{1}$	$Pna2_1$	$P2_1/n$
a (Å)	5.7165(8)	14.553(3)	3.5770(3)
b (Å)	6.8605(12)	22.849(4)	9.9954(6)
<i>c</i> (Å)	9.6419(13)	6.2866(12)	19.6856(18)
a (°)	89.357(12)		
β (°)	93.956(11)		94.508(8)
γ (°)	100.074(13)		
Volume (Å ³)	371.42(10)	2090.5(7)	701.65(10)
Ζ	2	4	4
F(000)	260	1320	532
$D_{\text{calcd.}} (\text{g cm}^{-3})$	2.387	2.142	2.613
Crystal size (mm)	$0.2\!\times\!0.1\!\times\!0.03$	$0.2 \times 0.1 \times 0.05$?
$T(\mathbf{K})$	293(2)	100	293(2)
2θ ranges (°)	3.02-26.09	2.80-26.09	2.91-26.00
No. reflections collected	3350	28431	6404
No. reflections observed	1442	4145	1381
$R_1, w R_2^{[a]}$	0.0416, 0.0575	0.0264, 0.0385	0.0187, 0.0376
Final difference (eÅ-3)	0.535, -0.521	0.919, -0.480	0.286, -0.339
Flack x ^[22]	-	-0.03(3)	_

[a] $R_1 = [\Sigma(||F_o| - |F_c|)/\Sigma|F_o|]; wR_2 = [\Sigma(w(F_o^2 - F_c^2)^2)/\Sigma(wF_o^4)]^{1/2}. S = [\Sigma w(F_o^2 - F_c^2)^2 n - pp]^{1/2}. n =$ number of reflections, p = parameters used.

δ = -8.4. (d, ${}^{1}J_{107}{}_{Ag^{31}P} = 447$ Hz), -8.4 (d, ${}^{1}J_{109}{}_{Ag^{31}P} = 516$ Hz) ppm. TGA (4 K/min): $T_{start} = 100$ °C, $T_{end} = 300$ °C, Δm = 81.1%.

Crystal Structure Determination: Crystal data for **5**, **6**, and **8** are presented in Table 5. All data were collected with a Oxford Gemini 5 diffractometer at 100(2) K by using Mo- K_a radiation ($\lambda = 0.71073$ Å). The structures were solved by direct methods by using SHELXS-97^[20] and refined by full-matrix least-square procedures on F^2 with SHELXL-97.^[21] All non-hydrogen atoms were refined anisotropically, and a riding model was employed in the refinement of the hydrogen atom positions. CCDC-704873 for **5**, CCDC-704875 for **6**, and CCDC-704874 for **8** contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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