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Phosphane- and phosphite-silver(I) phenolates: Synthesis, characterization and their use as CVD precursors

Alexander Jakob [a], Heike Schmidt [a], Bernhard Walfort [a], Tobias Rüffer [a], Thomas Haase [b], Katharina Kohse-Höinghaus [b], Heinrich Lang [a,*]

[a] Technische Universität Chemnitz, Fakultät für Naturwissenschaften, Institut für Chemie, Lehrstuhl für Anorganische Chemie, Straße der Nationen 62, 09111 Chemnitz, Germany
[b] Universität Bielefeld, Physikalische Chemie I, Postfach 100131, 33501 Bielefeld, Germany

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ABSTRACT

The silver(I) salts [AgOR] (**3a**, R = C_9H_6N; **3b**, R = C_6H_4-2-CHO, **3c**, R = C_6H_4-2-Cl; **3d**, R = C_6H_4-2-$C\equiv N$; **3e**, R = C_6H_4-2-NO_2) are accessible by the stoichiometric reaction of [$AgNO_3$] (**1**) with HOR (**2a**, R = C_9H_6N; **2b**, R = C_6H_4-2-CHO; **2c**, R = C_6H_4-2-Cl; **2d**, R = C_6H_4-2-$C\equiv N$; **2e**, R = C_6H_4-2-NO_2) in presence of NEt_3. Treatment of **3a**–**3e** with P^nBu_3 (**4**), $P(OMe)_3$ (**5a**) or $P(OCH_2CF_3)_3$ (**5b**) in the ratios of 1:1 and 1:2, respectively, produced complexes [L_mAgOR] (L = P^nBu_3, $m = 1$: **6a**, R = C_9H_6N; **6b**, R = C_6H_4-2-CHO; **6c**, R = C_6H_4-2-Cl; **6d**, R = C_6H_4-2-$C\equiv N$; **6e**, R = C_6H_4-2-NO_2. $m = 2$: **7a**, R = C_9H_4; **7b**, R = C_6H_4-2-CHO; **7c**, R = C_6H_4-2-Cl; **7d**, R = C_6H_4-2-$C\equiv N$; **7e**, R = C_6H_4-2-NO_2. L = $P(OMe)_3$, $m = 1$: **8a**, R = C_6H_4-2-CHO; **8b**, R = C_6H_4-2-NO_2. $m = 2$: **9**, R = C_6H_4-2-NO_2. L = $P(OCH_2CF_3)_3$, $m = 1$: **10**, R = C_6H_4-2-NO_2). Based on TGA, temperature-programmed and *in situ* molecular beam mass spectrometry metal–organic **7e** was applied as CVD precursor in the deposition of silver onto glass substrates. The resulting silver films were characterized by XRD. The SEM image of a film grown from **7e** at 350 °C showed a homogeneous surface with grain sizes of 40 nm. The molecular structures of **8b** and **10** in the solid state were determined. They are isostructural and are cubane-like structured. Low-temperature $^{31}P\{^1H\}$ NMR studies showed that the title complexes are dynamic in solution and exchange at room temperature their ligands.

1. Introduction

The growth of coinage metal films is of great interest with recent advances made in the deposition of copper, [1] silver, [2] and gold [3] using the CVD (= Chemical Vapor Deposition) process. Lately, silver becomes more valuable in the field of microelectronics, due to its lowest resistivity and highest thermal conductivity of all metals. [4] Further applications include, for example, the use of silver as a component of high-temperature superconducting ceramics [5], as silver mirrors [6], or as bactericidal coatings [7]. One of the mayor problems in silver-CVD is the availability of suitable precursors which are stable, volatile, and economical in their synthesis [8]. There have been several reports on the use of Lewis-base silver(I) β-diketonates as suitable CVD precursors [2a,9], however, to date new silver complexes which can be efficiently used for CVD deposition experiments are still not sufficiently available. In addition, the gas-phase deposition mechanism of such species is still not completely understood. Among thus, from the family of silver(I) phenolates only triphenyl-phosphane silver(I) phenolate, cresolate and trichlorophenolate have been reported by Molloy et al. to grow silver films on glass substrates using an aerosol-assisted chemical vapor deposition method [10]. The films produced are of poor quality and the respective precursors are solids.

This prompted us to prepare a series of novel phosphane and phosphite silver(I) phenolates and to apply them as possible CVD precursors for the deposition of silver on glass substrates. The thermal stability of these metal–organic complexes and the potential formation mechanism of silver-containing fragments in the gas-phase by temperature-programmed and *in situ* molecular beam mass spectrometry is reported as well.

2. Experimental

2.1. General information

All reactions were carried out under an atmosphere of purified nitrogen (O_2 traces: CuO catalyst, BASF AG, Ludwigshafen; H_2O: molecular sieve 4 Å, Aldrich Company) using standard Schlenk techniques. Dichloromethane and acetonitrile were purified by distillation from P_2O_5, diethyl ether and petroleum ether from sodium/benzophenone ketyl, and ethanol from sodium and diethylphthalate. Infrared spectra were recorded with a Perkin Elmer FT-IR spectrometer (Spectrum 1000) (KBr for solids and NaCl plates for liquids). ^1H NMR spectra were recorded with a Bruker Avance 250 spectrometer operating at 250.130 MHz in the Fourier

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* Corresponding author. Tel.: +49 (0)371 531 21210; fax: +49 (0)371 531 21219.
E-mail address: heinrich.lang@chemie.tu-chemnitz.de (H. Lang).

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transform mode. $^{13}C\{^1H\}$ NMR spectra were recorded at 62.895 MHz. Chemical shifts are reported in δ units (parts per million) downfield from tetramethylsilane (δ = 0.00 ppm) with the solvent as the reference signal (^{1}H NMR, $CDCl_3$, δ = 7.26; $^{13}C\{^1H\}$ NMR, $CDCl_3$, δ = 77.55). $^{31}P\{^1H\}$ NMR spectra were recorded at 101.255 MHz in $CDCl_3$ with $P(OMe)_3$ as external standard (δ = 139.0, rel. to H_3PO_4 (85%) with δ = 0.00). Thermogravimetric studies were carried out with the Perkin Elmer System Pyris TGA 6 with a constant heating rate of 8 K min^{-1} under N_2 (20.0 dm^3 h^{-1}). Microanalyses were performed by the Institute of Organic Chemistry, University of Heidelberg (Heraeus C, H ,N-Analyzer) and the Institute of Organic Chemistry, Chemnitz Technical University (Foss Heraeus Vario EL C, H, N-Analyzer). The melting (decomposition) points were determined with a Gallenkamp MFB 595 010 M melting point apparatus. For *in situ* mass spectrometric experiments, a molecular beam was extracted through a quartz nozzle from the deposition zone of a CVD reactor, expanded and investigated in a time-of-flight mass spectrometer. The precursor was evaporated using a pulsed spray evaporation technique and transported to the deposition zone (heated quartz tube, length 100 mm) at a pressure of 50 mbar. Argon was used as the carrier gas at a flow rate of 100 sccm. The electron impact ionization took place at a pressure of 10^{-6} mbar at the ionization energy of 30 eV [11]. The CVD experiments were performed in a vertical cold-wall reactor with stagnation point flow geometry. The precursor was introduced into the reactor using the pulsed spray evaporation technique. Glass (square, diameter 25 mm) was used as substrate. More details on the reactor setup can be found in reference [11].

2.2. Reagents

All reagents used in the synthesis of **3** and **6**–**10** were purchased from commercial suppliers and were used as received.

2.3. Synthesis of [$AgOC_9H_6N$] (**3a**) [**12a**]

8-Hydroxychinoline (**2a**) (1.16 g, 8.0 mmol) was dissolved in 30 mL of ethanol and triethylamine (810 mg, 8.0 mmol) was added in a single portion. This mixture was drop-wise added to [$AgNO_3$] (**1**) (1.36 g, 8.0 mmol) dissolved in 30 mL of ethanol and 3 mL of acetonitrile, respectively, at 0 °C. After stirring the reaction mixture for 2 h at this temperature, the precipitate was collected and was thoroughly washed with 10 mL of ethanol and three times with petroleum ether (20 mL). The yellow solid was dried in *oil-pump vacuum* giving 1.64 g (6.5 mmol, 81% based on **2a**) of the title complex. Complex **3a** is insoluble in common organic solvents.

Anal. Calc. for C_9H_6AgNO (252.01): C, 42.89; H, 2.40; N, 2.40. Found: C, 43.29; H, 2.69, N, 2.81%. Mp: 297 °C (decomp.). IR (KBr, cm^{-1}): $\tilde{\nu}$(CO) 1321 cm^{-1}.

2.4. Synthesis of [$AgOC_6H_4$-2-CHO] (**3b**)

Complex **3b** was synthesized in the same manner as **3a** (Section 2.3): Salicylaldehyde (**2b**) (0.72 g, 5.9 mmol), [$AgNO_3$] (**1**) (1.0 g, 5.9 mmol), and NEt_3 (0.60 g, 5.9 mmol). After appropriate work-up, **3b** could be isolated as a yellow, moisture and temperature sensitive solid. Yield: 0.22 g (1.0 mmol, 16% based on **2b**).

Anal. Calc. for $C_7H_5AgO_2$ (228.98): C, 36.56; H, 2.19. Found: C, 36.14; H, 2.16%. Mp: 116 °C (decomp.). IR (KBr, cm^{-1}): $\tilde{\nu}$ (CH) 2756, $\tilde{\nu}$ (CO) 1669, $\tilde{\nu}$ (C=C) 1600, 1525, $\tilde{\nu}$ (CO) 1149 cm^{-1}.

2.5. Synthesis of [$AgOC_6H_4$-2-Cl] (**3c**)

Complex **3c** was prepared as described for the preparation of **3a** (Section 2.3): 2-chlorophenol (**2c**) (0.76 g, 5.9 mmol), [$AgNO_3$] (**1**) (1.0 g, 5.9 mmol), and NEt_3 (0.60 g, 5.9 mmol). After appropriate work-up, **3c** could be isolated as a colorless, temperature and light sensitive solid which best should be stored at low temperature and in the dark. Yield: 0.36 g (1.5 mmol, 26% based on **2c**).

Anal. Calc. for C_6H_4AgClO (235.41): C, 30.61; H, 1.71. Found: C, 30.74; H, 1.73%. Mp: 73 °C (decomp.). IR (KBr, cm^{-1}): $\tilde{\nu}$ (C=C) 1576, 1469, $\tilde{\nu}$ (CO) 1309 cm^{-1}.

2.6. Synthesis of [$AgOC_6H_4$-2-$C\equiv N$] (**3d**)

Complex **3d** was synthesized as described for **3a** (Section 2.3): 2-Cyanophenol (**2d**) (1.79 g, 17.7 mmol), [$AgNO_3$] (**1**) (3.0 g, 17.7 mmol), and NEt_3 (1.79 g, 17.7 mmol). The silver(I) salt **3d** could be isolated as a colorless, temperature and light sensitive solid. Storage at low temperature and in the dark is recommended. Yield: 3.54 g (15.7 mmol, 88% based on **2d**).

Anal. Calc. for C_7H_4AgNO (225.98): C, 37.20; H, 1.78; N, 6.20. Found: C, 37.16; H, 1.74; N, 6.29%. Mp: 118 °C (decomp.). IR (KBr, cm^{-1}): $\tilde{\nu}$ ($C\equiv N$) 2209, $\tilde{\nu}$ ($C\equiv C$) 1596, 1539, $\tilde{\nu}$ (CO) 1274 cm^{-1}.

2.7. Synthesi of [$AgOC_6H_4$-2-NO_2] (**3e**) [**12b**]

Metal–organic **3e** was synthesized according to **3a** (Section 2.3) with following details: 2-nitrophenol (**2e**) (1.80 g, 17.8 mmol), [$AgNO_3$] (**1**) (3.02 g, 17.8 mmol), and NEt_3 (1.80 g, 17.8 mmol). After appropriate work-up, **3e** could be isolated as an orange-red solid. Yield: 3.09 g (12.6 mmol, 71% based on **2e**).

Mp: 67 °C (decomp.). IR: $\tilde{\nu}$ ($C\equiv C$) 1610, 1538, $\tilde{\nu}$ (NO) 1495, 1324, $\tilde{\nu}$ (CO) 1243 cm^{-1}. ^{1}H NMR (CD_3CN): δ 6.36 (dd, 1 H, H^3, $^3J_{HH}$ = 7.6 Hz, $^3J_{HH}$ = 7.6 Hz), 6.78 (d, 1 H, H^4, $^3J_{HH}$ = 9.0 Hz), 7.22 (ddd, 1 H, H^2, $^3J_{HH}$ = 8.8 Hz, $^3J_{HH}$ = 6.9 Hz, $^4J_{HH}$ = 1.9 Hz), 7.82 (dd, 1 H, H^1, $^3J_{HH}$ = 8.4 Hz, $^4J_{HH}$ = 1.9 Hz). Please, notice that due to the high thermal instability of **3e** no satisfying elemental analysis could be obtained. It is advised to store **3e** low temperature to prevent significant decomposition!

2.8. Synthesis of [$^nBu_3PAgOC_9H_6N$] (**6a**)

$^nBu_3P$ (**4**) (510 mg, 2.5 mmol) was added in a single portion to **3a** (640 mg, 2.6 mmol, 2% excess based on **4**) suspended in 40 mL of diethyl ether at 25 °C. After stirring the reaction mixture for 2 h at this temperature it was filtered through a pad of Celite. Removal of all volatiles in *oil-pump vacuum* produced a yellow solid. Yield: 1.12 g (2.5 mmol, 98% based on **4**).

Anal. Calc. for $C_{21}H_{33}AgNOP$ (454.32): C, 55.51; H, 7.32; N, 3.08. Found: C, 54.98; H, 7.29; N, 3.09%. Mp: 28 °C. IR (KBr, cm^{-1}): ν(C=C) 1592, $\tilde{\nu}$ (CO), 1318 cm^{-1}. ^{1}H NMR ($CDCl_3$): δ 0.93 (t, 9 H, CH_3, J_{HH} = 7.0 Hz), 1.39–1.75 (m, 18 H, $CH_2CH_2CH_2CH_3$), 6.86 (dd, 1 H, H^1, $^3J_{HH}$ = 7.0 Hz, $^4J_{HH}$ = 1.0 Hz), 7.03 (dd, 1 H, H^3, $^3J_{HH}$ = 8.0 Hz, $^4J_{HH}$ = 1.0 Hz), 7.30 (dd, 1 H, H^5, $^3J_{HH}$ = 4.0 Hz, $^4J_{HH}$ = 8.0 Hz), 7.41 (dd, 1 H, H^2, $^3J_{HH}$ = 8.0 Hz, $^4J_{HH}$ = 8.0 Hz), 8.12 (dd, 1 H, H^4, $^3J_{HH}$ = 8.0 Hz, $^4J_{HH}$ = 2.0 Hz), 8.46 (dd, 1 H, H^6, $^3J_{HH}$ = 4.0 Hz, $^4J_{HH}$ = 2.0 Hz). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 13.7 (CH_3), 24.3 (d, $^3J_{CP}$ = 15.0 Hz, $CH_2CH_2CH_2CH_3$), 25.9 (d, $^2J_{CP}$ = 20.0 Hz, $CH_2CH_2CH_2CH_3$), 28.2 (d, $^1J_{CP}$ = 5.0 Hz, $CH_2CH_2CH_2CH_3$), 109.5 (C7), 113.8 (C5), 129.9 (C6), 130.5 (C4), 137.7 (C3), 141.6 (C9), 146.0 (C1), 164.4 (C8). $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ -3.0. TG: T_{begin} = 130 °C, T_{end} = 400 °C, Δm = 75.8%.

2.9. Synthesis of [$^nBu_3PAgOC_6H_4$-2-CHO] (**6b**)

Complex **6b** was prepared using the same synthesis methodology as described for **6a** (Section 2.8), however, as solvent dichloromethane was used: $^nBu_3P$ (**4**) (259 mg, 1.3 mmol), **3b** (300 mg, 1.3 mmol, 2% excess based on **4**). After appropriate work-up, **6b** could be isolated as pale yellow oil which best should be stored at −30 °C, otherwise decomposition may occur. Yield: 489 mg (1.2 mmol, 89% based on **4**).

Anal. Calc. for $C_{19}H_{32}AgO_2P$ (432.28) C, 52.91; H, 7.48. Found: C, 52.73; H, 7.67%. IR (NaCl, cm^{-1}): $\tilde{\nu}$ (CH) 2712 $\tilde{\nu}$ (CO) 1673, $\tilde{\nu}$ (C=C) 1596, 1530, $\tilde{\nu}$ (CO) 1143 cm^{-1}. ^1H NMR ($CDCl_3$): δ 0.90 (t, 9 H, CH_3, $J_{HH} = 7.0$ Hz), 1.31–1.73 (m, 18 H, $\mathit{CH_2CH_2CH_2}CH_3$), 6.54 (ddd, 1 H, H^3, $^3J_{HH} = 7.3$ Hz, $^3J_{HH} = 7.3$ Hz, $^4J_{HH} = 1.0$ Hz), 6.76 (d, 1 H, H^1, $^3J_{HH} = 8.5$ Hz), 7.20–7.35 (m, 2 H, H^2, H^4), 9.73 (bs, 1 H, CHO). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 13.7 (CH_3), 24.3 (d, $^3J_{CP} = 14.0$ Hz, $CH_2CH_2\mathit{CH_2}CH_3$), 25.9 (d, $^2J_{CP} = 22.0$ Hz, $CH_2\mathit{CH_2}CH_2CH_3$), 27.9 (d, $^1J_{CP} = 4.0$ Hz, $\mathit{CH_2}CH_2CH_2CH_3$), 113.7 (C6), 123.5 (C4), 135.8 (C3), 144.3 (C5), 194.5 (CHO). $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ −0.5 (bd, $^1J_{107Ag31P} = 700$ Hz), −0.5 (bd, $^1J_{109Ag31P} = 775$ Hz).

2.10. Synthesis of [$^nBu_3PAgOC_6H_4$-2-Cl] (**6c**)

Complex **6c** was synthesized as described for the preparation of **6a** (Section 2.8) in dichloromethane as solvent: $^nBu_3P$ (**4**) (23 mg, 0.6 mmol), **3c** (146 mg, 0.6 mmol, 2% excess based on **4**). After appropriate work-up, **6c** could be isolated as a colorless solid which should best be stored at −30 °C, otherwise decomposition upon formation of elemental silver may occur. Yield: 184 mg (0.4 mmol, 68% based on **4**).

Anal. Calc. for $C_{18}H_{31}AgClOP$ (437.73): C, 49.39; H, 7.14. Found: C, 49.06; H, 7.24%. Mp: 63 °C (decomp.). IR (KBr, cm^{-1}): $\tilde{\nu}$ (C=C) 1576, 1468, $\tilde{\nu}$ (CO) 1310 cm^{-1}. ^1H NMR ($CDCl_3$): δ 0.93 (t, 9 H, CH_3, $J_{HH} = 7.1$ Hz), 1.34–1.74 (m, 18 H, $\mathit{CH_2CH_2CH_2}CH_3$), 6.44 (ddd, 1 H, H^2, $^3J_{HH} = 7.6$ Hz, $^3J_{HH} = 7.2$ Hz, $^4J_{HH} = 1.6$ Hz), 6.88 (dd, 1 H, H^1, $^3J_{HH} = 8.1$ Hz, $^4J_{HH} = 1.8$ Hz), 7.04 (ddd, 1 H, H^3, $^3J_{HH} = 8.1$ Hz, $^3J_{HH} = 7.2$ Hz, $^4J_{HH} = 1.8$ Hz) 7.24 (dd, 1 H, H^4, $^3J_{HH} = 8.0$ Hz, $^4J_{HH} = 1.8$ Hz). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 13.8 (CH_3), 24.4 (d, $^3J_{CP} = 14.0$ Hz, $CH_2CH_2\mathit{CH_2}CH_3$), 25.3 (d, $^2J_{CP} = 26.0$ Hz, $CH_2\mathit{CH_2}CH_2CH_3$), 27.9 ($\mathit{CH_2}CH_2CH_2CH_3$), 114.1 (C6), 120.8 (C2), 121.0 (C4), 128.2 (C5), 129.1 (C3), 157.0 (C1). $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ 0.7 (d, $^1J_{107Ag31P} = 656$ Hz), 0.7 (d, $^1J_{109Ag31P} = 755$ Hz). TG: $T_{begin} = 142$ °C, $T_{end} = 383$ °C, $\Delta m = 66.2\%$; $T_{begin} = 516$ °C, $T_{end} = 672$ °C, $\Delta m = 2.8\%$.

2.11. Synthesis of [$^nBu_3PAgOC_6H_4$-2-C≡N] (**6d**)

Complex **6d** was synthesized in the same manner as **6a** (Section 2.8): Solvent dichloromethane, $^nBu_3P$ (**4**) (0.89 g, 4.4 mmol), **3d** (1.01 g, 4.5 mmol, 2% excess based on **4**). After appropriate work-up, **6d** could be isolated as an off-white solid. Yield: 1.64 g (3.83 mmol, 87% based on **4**). Storage at −30 °C is advisable to prevent significant decomposition.

Anal. Calc. for $C_{19}H_{31}AgNOP$ (428.29): C, 53.28; H, 7.30; N, 3.27. Found: C, 52.93; H, 7.36; N, 3.26%. Mp: 35 °C. IR (KBr, cm^{-1}): $\tilde{\nu}$ (C≡N) 2207, $\tilde{\nu}$ (C=C) 1598, 1538, 1472, $\tilde{\nu}$ (CO) 1275 cm^{-1}. ^1H NMR ($CDCl_3$): δ 0.91 (t, 9 H, CH_3, $J_{HH} = 7.0$ Hz), 1.30–1.76 (m, 18 H, $\mathit{CH_2CH_2CH_2}CH_3$), 6.47 (ddd, 1 H, H^2, $^3J_{HH} = 8.0$ Hz, $^3J_{HH} = 7.0$ Hz, $^4J_{HH} = 1.0$ Hz), 6.80 (dd, 1 H, H^4, $^3J_{HH} = 8.5$ Hz, $^4J_{HH} = 0.3$ Hz), 7.25 (ddd, 1 H, H^3, $^3J_{HH} = 8.7$ Hz, $^3J_{HH} = 7.0$ Hz, $^4J_{HH} = 1.9$ Hz) 7.32 (dd, 1 H, H^1, $^3J_{HH} = 7.6$ Hz, $^4J_{HH} = 1.9$ Hz). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 13.8 (CH_3), 24.4 (d, $^3J_{CP} = 15.0$ Hz, $CH_2CH_2\mathit{CH_2}CH_3$), 24.8 (d, $^2J_{CP} = 20.0$ Hz, $CH_2\mathit{CH_2}CH_2CH_3$), 27.8 ($\mathit{CH_2}CH_2CH_2CH_3$), 99.6 (C2), 113.9 (C≡N), 120.9 (C6), 121.9 (C4), 132.5 (C3), 134.3 (C5), 172.1 (C1). $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ 0.2 (d, $^1J_{107Ag31P} = 677$ Hz), 0.2 (d, $^1J_{109Ag31P} = 780$ Hz).

2.12. Synthesis of [$^nBu_3PAgOC_6H_4$-2-NO_2] (**6e**)

Complex **6e** was prepared as described in Section 2.8: Solvent dichloromethane, $^nBu_3P$ (**4**) (132 mg, 0.7 mmol), **3e** (164 mg, 0.7 mmol, 2% excess based on **4**). After appropriate work-up, **6e** could be isolated as an orange solid. Yield: 267 mg (0.6 mmol, 91% based on **4**). It is advisable to store **6e** at −30 °C to provide decomposition.

Anal. Calc. for $C_{18}H_{31}AgNO_3P$ (448.28): C, 48.23; H, 6.97; N, 3.13. Found: C, 48.83; H, 7.22; N, 3.07%. Mp: 54 °C. IR (KBr, cm^{-1}): $\tilde{\nu}$ (C=C) 1614, 1545, $\tilde{\nu}$ (NO) 1504, 1334, $\tilde{\nu}$ (CO) 1251 cm^{-1}. ^1H NMR ($CDCl_3$): δ 0.90 (t, 9 H, CH_3, $J_{HH} = 7.0$ Hz), 1.30–1.73 (m, 18 H, $\mathit{CH_2CH_2CH_2}CH_3$), 6.46 (ddd, 1 H, H^2, $^3J_{HH} = 8.4$ Hz, $^3J_{HH} = 6.8$ Hz, $^4J_{HH} = 1.3$ Hz), 6.92 (dd, 1 H, H^4, $^3J_{HH} = 8.5$ Hz, $^4J_{HH} = 1.3$ Hz), 7.21 (ddd, 1 H, H^3, $^3J_{HH} = 8.6$ Hz, $^3J_{HH} = 6.8$ Hz, $^4J_{HH} = 1.9$ Hz) 7.94 (dd, 1 H, H^1, $^3J_{HH} = 8.6$ Hz, $^4J_{HH} = 1.9$ Hz). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 14.0 (CH_3), 24.4 (d, $^3J_{CP} = 15.0$ Hz, $CH_2CH_2\mathit{CH_2}CH_3$), 25.2 (d, $^2J_{CP} = 22.0$ Hz, $CH_2\mathit{CH_2}CH_2CH_3$), 28.0 ($\mathit{CH_2}CH_2CH_2CH_3$), 113.8 (C6), 126.5 (C4), 126.7 (C3), 135.4 (C2), 138.2 (C5). $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ 0.2 (d, $^1J_{107Ag31P} = 689$ Hz), 0.2 (d, $^1J_{109Ag31P} = 785$ Hz). TG: $T_{begin} = 102$ °C, $T_{end} = 208$ °C, $\Delta m = 18.0\%$; $T_{begin} = 208$ °C, $T_{end} = 349$ °C, $\Delta m = 43.1\%$; $T_{begin} = 349$ °C, $T_{end} = 529$ °C, $\Delta m = 2.1\%$; $T_{begin} = 529$ °C, $T_{end} = 877$ °C, $\Delta m = 7.1\%$. DSC: Peak 218 °C, $\Delta H = -423.3$ J/g; Peak 285 °C, $\Delta H = 50.3$ J/g.

2.13. Synthesis of [($^nBu_3P)_2AgOC_9H_6N$] (**7a**)

$^nBu_3P$ (**4**) (610 mg, 3.0 mmol) was added in a single portion to **3a** (390 mg, 1.5 mmol) suspended in 40 mL of diethyl ether at 25 °C. After the reaction mixture was stirred for 2 h at this temperature it was filtrated through a pad of Celite. Removal of all volatiles in *oil-pump vacuum* produced **7a** as orange oil. Yield: 945 mg (1.4 mmol, 96% based on **3a**).

Anal. Calc. for $C_{33}H_{60}AgNOP_2$ (656.66) C, 60.36; H, 9.21; N, 2.13. Found: C, 60.04; H, 9.25; N, 2.30%. IR (NaCl, cm^{-1}): $\tilde{\nu}$ (C=C) 1593, $\tilde{\nu}$ (CO), 1332 cm^{-1}. ^1H NMR ($CDCl_3$): δ 0.80 (t, 18 H, CH_3, $J_{HH} = 7.0$ Hz), 1.22–1.51 (m, 36 H, $\mathit{CH_2CH_2CH_2}CH_3$), 6.85 (dd, 1 H, H^1, $^3J_{HH} = 8.0$ Hz, $^4J_{HH} = 1.0$ Hz), 6.99 (dd, 1 H, H^3, $^3J_{HH} = 8.0$ Hz, $^4J_{HH} = 1.0$ Hz), 7.22 (dd, 1 H, H^5, $^3J_{HH} = 4.0$ Hz, $^4J_{HH} = 8.0$ Hz), 7.33 (dd, 1 H, H^2, $^3J_{HH} = 8.0$ Hz, $^4J_{HH} = 8.0$ Hz), 8.03 (dd, 1 H, H^4, $^3J_{HH} = 8.0$ Hz, $^4J_{HH} = 2.0$ Hz), 8.46 (dd, 1 H, H^6, $^3J_{HH} = 4.0$ Hz, $^4J_{HH} = 2.0$ Hz). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 13.5 (CH_3), 24.3 (d, $^3J_{CP} = 13.0$ Hz, $CH_2CH_2\mathit{CH_2}CH_3$), 25.8 (d, $^2J_{CP} = 7.0$ Hz, $CH_2\mathit{CH_2}CH_2CH_3$), 27.4 (d, $^1J_{CP} = 8.0$ Hz, $\mathit{CH_2}CH_2CH_2CH_3$), 109.7 (C3), 113.0 (C5), 120.0 (C8), 128.8 (C4), 130.3 (C6), 136.0 (C7), 141.9 (C1), 145.1 (C9), 162.7 (C2). $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ -3.0. TG: $T_{begin} = 100$ °C, $T_{end} = 350$ °C, $\Delta m = 83.2\%$.

2.14. Synthesis of [($^nBu_3P)_2AgOC_6H_4$-2-CHO] (**7b**)

Complex **7b** was synthesized as described for **7a** (Section 2.13): dichloromethane, $^nBu_3P$ (**4**) (320 mg, 1.6 mmol), and **3b** (187 mg, 0.8 mmol). After appropriate work-up, **7b** could be isolated as yellow oil. Yield: 481 mg (0.8 mmol, 92% based on **3b**). It is advisable to store **7b** at −30 °C to prevent decomposition to elemental silver.

Anal. Calc. for $C_{31}H_{59}AgO_2P_2$ (645.63): C, 59.53; H, 9.21. Found: C, 59.57; H, 9.86%. IR (NaCl, cm^{-1}): $\tilde{\nu}$ (CH) 2712, $\tilde{\nu}$ (CO) 1645, $\tilde{\nu}$ (C=C) 1599, 1524, $\tilde{\nu}$ (CO) 1141 cm^{-1}. ^1H NMR ($CDCl_3$): δ 0.87 (t, 18 H, CH_3, $J_{HH} = 7.0$ Hz), 1.26–1.65 (m, 36 H, $\mathit{CH_2CH_2CH_2}CH_3$), 6.45 (dd, 1 H, H^3, $^3J_{HH} = 7.3$ Hz, $^3J_{HH} = 7.3$ Hz), 6.70 (d, 1 H, H^1, $^3J_{HH} = 8.5$ Hz), 7.21 (ddd, 1 H, H^2, $^3J_{HH} = 7.7$ Hz, $^3J_{HH} = 7.7$ Hz, $^4J_{HH} = 1.9$ Hz), 7.46 (dd, 1 H, H^4, $^3J_{HH} = 7.9$ Hz, $^4J_{HH} = 1.9$ Hz), 10.15 (1 H, CHO). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 13.8 (CH_3), 24.5 (d, $^3J_{CP} = 12.0$ Hz, $CH_2CH_2\mathit{CH_2}CH_3$), 25.1 (d, $^2J_{CP} = 13.0$ Hz, $CH_2\mathit{CH_2}CH_2CH_3$), 27.7 ($\mathit{CH_2}CH_2CH_2CH_3$); further resonance signals could not be detected, due to the low stability of **7b**. $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ 0.2. TG: $T_{begin} = 103$ °C, $T_{end} = 239$ °C, $\Delta m = 50.9\%$; $T_{begin} = 239$ °C, $T_{end} = 289$ °C, $\Delta m = 1.3\%$; $T_{begin} = 289$ °C, $T_{end} = 886$ °C, $\Delta m = 7.6\%$.

2.15. Synthesis of [($^nBu_3P)_2AgOC_6H_4$-2-Cl] (**7c**)

Complex **7c** was synthesized as described in Section 2.13: dichloromethane, $^nBu_3P$ (**4**) (158 mg, 0.8 mmol), **3c**, (92 mg, 0.4 mmol). After appropriate work-up, **7c** could be isolated as off-white oil. Storage at −30 °C is advised (vide supra). Yield: 247 mg (0.4 mmol, 99% based on **3c**).

Anal. Calc. for $C_{30}H_{58}AgClOP_2 \times 2/3\ CH_2Cl_2$ (640.04): C, 52.65; H, 8.55. Found: C, 52.60; H, 8.61%. IR (NaCl, cm^{-1}): $\tilde{\nu}$ (C=C) 1575, 1466, $\tilde{\nu}$ (CO) 1316 cm^{-1}. ^1H NMR ($CDCl_3$): δ 0.85 (t, 18 H, CH_3, J_{HH} = 7.0 Hz), 1.27–1.68 (m, 36 H, $CH_2CH_2CH_2CH_3$), 5.28 (2 H, CH_2Cl_2), 6.43 (ddd, 1 H, H^2, $^3J_{HH}$ = 7.8 Hz, $^3J_{HH}$ = 6.3 Hz, $^4J_{HH}$ = 1.5 Hz), 6.88–7.00 (m, 2 H, H^3, H^4), 7.19 (dd, 1 H, H^1, $^3J_{HH}$ = 7.1 Hz, $^4J_{HH}$ = 1.5 Hz). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 13.8 (CH_3), 24.5 (d, $^3J_{CP}$ = 13.0 Hz, $CH_2CH_2CH_2CH_3$), 25.0 (d, $^2J_{CP}$ = 17.0 Hz, $CH_2CH_2CH_2CH_3$), 27.8 ($CH_2CH_2CH_2CH_3$), 53.5 (CH_2Cl_2), 115.4 (C6), 119.9 (C2), 121.9 (C4), 128.2 (C5), 129.5 (C3). $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ −5.8.

2.16. Synthesis of $[(^nBu_3P)_2AgOC_6H_4\text{-2-}C{\equiv}N]$ (**7d**)

Complex **7d** was prepared as described in Section 2.13: $^nBu_3P$ (**4**) (1.72 g, 8.5 mmol), **3d**, (962 mg, 4.3 mmol). **7d** could be isolated as yellow-brown oil which should be stored at 0 °C to prevent decomposition. Yield: 2.41 g (3.8 mmol, 90% based on **3d**).

Anal. Calc. for $C_{31}H_{58}AgNOP_2 \times 0.2\ CH_2Cl_2$ (630.60): C, 57.86; H, 9.09; N, 2.16. Found: C, 57.90; H, 9.43; N, 2.80%. IR (NaCl, cm^{-1}): $\tilde{\nu}$ (C≡N) 2204, $\tilde{\nu}$ (C=C) 1594, 1533, 1470, $\tilde{\nu}$ (CO) 1277 cm^{-1}. ^1H NMR ($CDCl_3$): δ 0.78 (t, 18 H, CH_3, J_{HH} = 7.0 Hz), 1.17–1.60 (m, 36 H, $CH_2CH_2CH_2CH_3$), 5.19 (2 H, CH_2Cl_2), 6.11 (dd, 1 H, H^2, $^3J_{HH}$ = 7.3 Hz, $^3J_{HH}$ = 7.3 Hz), 6.51 (d, 1 H, H^4, $^3J_{HH}$ = 8.5 Hz),7.00 (ddd, 1 H, H^3, $^3J_{HH}$ = 7.8 Hz, $^3J_{HH}$ = 7.8 Hz, $^4J_{HH}$ = 1.9 Hz), 7.10 (dd, 1 H, H^1, $^3J_{HH}$ = 7.8 Hz, $^4J_{HH}$ = 1.8 Hz). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 13.6 (CH_3), 24.3 (bs, $CH_2CH_2CH_2CH_3$), 24.8 (bs, $CH_2CH_2CH_2CH_3$), 27.4 ($CH_2CH_2CH_2CH_3$), 53.4 (CH_2Cl_2), 98.9 (C2), 110.9 (C≡N), 121.1 (C6), 122.6 (C4), 132.5 (C3), 133.3 (C5), C1 could not be detected under the measurement conditions applied. $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ −7.1.

2.17. Synthesis of $[(^nBu_3P)_2AgOC_6H_4\text{-2-}NO_2]$ (**7e**)

For details of synthesizing **7e** see Section 2.13: $^nBu_3P$ (**4**) (386 mg, 1.9 mmol), **3e** (235 mg, 1.0 mmol). After appropriate work-up, **7e** could be isolated as red oil. Complex **7e** should best be stored at 0 °C otherwise decomposition may occur upon formation of elemental silver. Yield: 611 mg (0.9 mmol, 98% based on **3e**).

Anal. Calc. for $C_{30}H_{58}AgNO_3P_2$ (650.59): C, 55.38; H, 8.99; N, 2.15. Found: C, 55.16; H, 9.24; N, 1.94%. IR (NaCl, cm^{-1}): $\tilde{\nu}$ (C=C) 1603, 1536, $\tilde{\nu}$ (NO) 1503, 1324, $\tilde{\nu}$ (CO) 1248 cm^{-1}. ^1H NMR ($CDCl_3$): δ 0.86 (t, 18 H, CH_3, J_{HH} = 6.9 Hz), 1.24–1.61 (m, 36 H, $CH_2CH_2CH_2CH_3$), 6.11 (dd, 1 H, H^4, $^3J_{HH}$ = 7.8 Hz, $^3J_{HH}$ = 7.8 Hz), 6.66 (dd, 1 H, H^3, $^3J_{HH}$ = 8.7 Hz, $^4J_{HH}$ = 1.0 Hz), 7.04 (ddd, 1 H, H^2, $^3J_{HH}$ = 8.7 Hz, $^3J_{HH}$ = 6.7 Hz, $^4J_{HH}$ = 1.9 Hz), 7.84 (dd, 1 H, H^1, $^3J_{HH}$ = 8.6 Hz, $^4J_{HH}$ = 1.9 Hz). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 13.8 (CH_3), 24.5 (bs, $CH_2CH_2CH_2CH_3$), 25.0 (bs, $CH_2CH_2CH_2CH_3$), 27.4 ($CH_2CH_2CH_2CH_3$), 110.9 (C6), 127.1 (C4), 127.9 (C3), 134.3 (C2), 136.8 (C5), 169.9 (C1). $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ −7.4. TG: T_{begin} = 121 °C, T_{end} = 216 °C, Δm = 38.9%; T_{begin} = 216 °C, T_{end} = 276 °C, Δm = 34.8%; T_{begin} = 276 °C, T_{end} = 867 °C, Δm = 7.1%. DSC: Peak 216 °C, ΔH = −492.1 J/g; Peak 299 °C, ΔH = 77.1 J/g.

2.18. Synthesis of $[(MeO)_3PAgOC_6H_4\text{-2-}CHO]$ (**8a**)

For the synthesis of complex **8a** see Section 2.13: $(MeO)_3P$ (**5a**) (113 mg, 0.9 mmol), **3a** (220 mg, 1.0 mmol, 2% excess based on **5a**). After appropriate work-up, **8a** could be isolated as a yellow solid. It is advisable to store **8a** at −30 °C to prevent decomposition into silver. Yield: 269 mg (0.8 mmol, 84% based on **5a**).

Anal. Calc. for $C_{10}H_{14}AgO_5P$ (354.04): C, 33.92; H, 3.99. Found: C, 33.83; H, 3.94%. IR (KBr, cm^{-1}): $\tilde{\nu}$ (CH) 2756, $\tilde{\nu}$ (CO) 1671, $\tilde{\nu}$ (C=C) 1592, 1527, $\tilde{\nu}$ (CO) 1148 cm^{-1}. ^1H NMR ($CDCl_3$): δ 3.70 (d, 9 H, CH_3, $^3J_{PH}$ = 13.6 Hz), 6.55 (ddd, 1 H, H^3, $^3J_{HH}$ = 7.9 Hz, $^3J_{HH}$ = 6.9 Hz, $^4J_{HH}$ = 1.0 Hz), 6.76 (dd, 1 H, H^1, $^3J_{HH}$ = 8.0 Hz, $^4J_{HH}$ = 1.0 Hz), 7.24–7.34 (m, 2 H, H^2, H^4), 9.62 (bs, 1 H, CHO). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 51.7 (d, CH_3, $^2J_{CP}$ = 5.0 Hz), 113.8 (C6), 123.3 (C2), 124.0 (C4), 136.2 (C5), 137.2 (C3), 195.2 (CHO); C1 could not be detected under the conditions of the measurement applied. $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ 131.3 (bs).

2.19. Synthesis of $[(MeO)_3PAgOC_6H_4\text{-2-}NO_2]$ (**8b**)

Complex **8b** was synthesized in the same manner as described earlier for **7a** (Section 2.13): $(MeO)_3P$ (**5a**) (230 mg, 1.9 mmol), **3e** (467 mg, 1.9 mmol, 2% excess based on **5a**). After appropriate work-up, **8b** could be isolated as a yellow solid. Yield: 481 mg (1.3 mmol, 70% based on **5a**). Storage at 0 °C is advisable to prevent decomposition.

Anal. Calc. for $C_9H_{13}AgNO_6P$ (369.98) C, 29.21; H, 3.54; N, 3.79. Found: C, 29.20; H, 3.55; N, 3.54%. IR (KBr, cm^{-1}): $\tilde{\nu}$ (C=C) 1610, 1540, $\tilde{\nu}$ (NO) 1499, 1326, $\tilde{\nu}$ (CO) 1244 cm^{-1}. ^1H NMR ($CDCl_3$): δ 3.54 (d, 9 H, CH_3, $^3J_{PH}$ = 4.0 Hz), 6.46 (ddd, 1 H, H^2, $^3J_{HH}$ = 8.4 Hz, $^3J_{HH}$ = 6.8 Hz, $^4J_{HH}$ = 1.5 Hz), 7.00 (dd, 1 H, H^4, $^3J_{HH}$ = 8.6 Hz, $^4J_{HH}$ = 1.9 Hz), 7.21 (ddd, 1 H, H^3, $^3J_{HH}$ = 7.7 Hz, $^3J_{HH}$ = 7.7 Hz, $^4J_{HH}$ = 1.9 Hz), 7.93 (dd, 1 H, H^1, $^3J_{HH}$ = 8.5 Hz, $^4J_{HH}$ = 1.8 Hz). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 51.5 (CH_3), 114.0 (C3), 126.7 (C6), 126.9 (C4), 135.4 (C2), 137.9 (C5), 167.2 (C1). $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ 129.9. TG: T_{begin} = 105 °C, T_{end} = 239 °C, Δm = 50.9%; T_{begin} = 239 °C, T_{end} = 289 °C, Δm = 1.3%; T_{begin} = 289 °C, T_{end} = 886 °C, Δm = 7.6%.

2.20. Synthesis of $[((MeO)_3P)_2AgOC_6H_4\text{-2-}NO_2]$ (**9**)

For the synthesis of **9** see Section 2.13: $(MeO)_3P$ (**5a**): (119 mg, 1.0 mmol), **3e** (118 mg, 0.5 mmol). After appropriate work-up, the title compound could be isolated as red oil. Yield: 202 mg (0.4 mmol, 85% based on **3e**). Storage at −30 °C is advisable due to significant decomposition to elemental silver may be observed.

Anal. Calc. for $C_{12}H_{22}AgNO_9P_2$ (494.11): C, 29.17; H, 4.49; N, 2.84. Found: C, 29.67; H, 4.44; N, 3.15%. IR (NaCl, cm^{-1}): $\tilde{\nu}$ (C=C) 1601, 1545, $\tilde{\nu}$ (NO) 1494, 1332, $\tilde{\nu}$ (CO) 1249 cm^{-1}. ^1H NMR ($CDCl_3$): δ 3.64 (d, 18 H, CH_3, $^3J_{PH}$ = 12.8 Hz), 6.47 (dd, 1 H, H^2, $^3J_{HH}$ = 7.8 Hz, $^3J_{HH}$ = 7.7 Hz), 6.89 (dd, 1 H, H^4, $^3J_{HH}$ = 8.8 Hz, $^4J_{HH}$ = 1.0 Hz), 7.28 (ddd, 1 H, H^3, $^3J_{HH}$ = 6.0 Hz, $^3J_{HH}$ = 6.0 Hz, $^4J_{HH}$ = 1.9 Hz), 7.96 (dd, 1 H, H^1, $^3J_{HH}$ = 8.8 Hz, $^4J_{HH}$ = 1.9 Hz). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 51.3 (d, CH_3, $^2J_{CP}$ = 5.0 Hz), 114.1 (C6), 126.0 (C4), 126.6 (C3), 135.6 (C5), 136.7 (C2), 166.3 (C1). $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ 131.6.

2.21. Synthesis of $[(CF_3CH_2O)_3PAgOC_6H_4\text{-2-}NO_2]$ (**10**)

Complex **10** was prepared as described in Section 2.13: $(CF_3CH_2O)_3P$ (**5b**) (170 mg, 1.2 mmol), **3e** (134 mg, 0.4 mmol, 2% excess based on **5b**). After appropriate work-up, **10** could be isolated as a yellow solid. Yield: 276 mg (0.5 mmol, 93% based on **5b**). Storage at 0 °C is advisable otherwise decomposition may occur to give elemental silver.

Anal. Calc. for $C_{12}H_{10}AgF_9NO_6P$ (574.04): C, 25.11; H, 1.76; N, 2.44. Found: C, 24.25; H, 1.98; N, 2.58%. Mp: 108 °C. IR (KBr, cm^{-1}): $\tilde{\nu}$ (C=C) 1612, 1540, $\tilde{\nu}$ (NO) 1499, 1331, $\tilde{\nu}$ (CO) 1244 cm^{-1}. ^1H NMR ($CDCl_3$): δ 3.90–4.20 (m, 6 H, CH_2), 6.73 (dd, 1 H, H^2, $^3J_{HH}$ = 7.5 Hz, $^3J_{HH}$ = 7.5 Hz), 7.16 (d, 1 H, H^4, $^3J_{HH}$ = 8.5 Hz), 7.39 (dd, 1 H, H^3, $^3J_{HH}$ = 7.7 Hz, $^3J_{HH}$ = 7.7 Hz), 7.97 (dd, 1 H, H^1, $^3J_{HH}$ = 8.5 Hz, $^4J_{HH}$ = 1.5 Hz). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 61.7 (qd, CH_2, $^2J_{CF}$ = 38.0 Hz, $^2J_{Cp}$ = 5.0 Hz), 116.4 (C3), 122.5 (q, CF_3, $^1J_{CF}$ = 269.0 Hz), 126.3 (C4), 126.8 (C5), 136.3 (C3); C1 and C2 could not be detected under the measurement conditions performed. $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ 127.9.

2.22. X-ray crystallography of **8b** and **10**

The preparation of suitable single crystals was done in perfluoroalkyl ether 216 (Riedel-de Haën) for protection against air and moisture. Data were collected with a Bruker AXS Smart 1k CCD diffractometer at 183 K (**8b**) and 298 K (**10**). Mo Kα radiation ($\lambda = 0.71073$ Å) was used. The structures were solved by direct methods using SHELXS-97, [13,14] and refined by full-matrix least-squares procedures on F^2 using SHELXL-97. [15] All *non*-hydrogen atoms were refined anisotropycally. All hydrogen atoms were refined using a riding model. In **10** five CH_2CF_3 groups of the $P(OCH_2CF_3)_3$ ligands are disordered and have been refined to split occupancies of 0.80/0.20 (C13, C14, F1–F3), 0.56/0.44 (C15, C16, F4–F6), 0.57/0.43 (C17, C18, F7–F9), 0.54/0.46 (C19, C20, F10–F12) and 0.54/0.46 (C23, C24, F16–F18), respectively. The asymmetric unit contains in both structures half of the tetramer.

Table 1
Complexes **6–10**.

Compd.	L	*m*	R	Yield[a] (%)
6a	P^nBu_3	1	C_9H_6N	98
6b	P^nBu_3	1	C_6H_4-2-CHO	89
6c	P^nBu_3	1	C_6H_4-2-Cl	68
6d	P^nBu_3	1	C_6H_4-2-$C{\equiv}N$	87
6e	P^nBu_3	1	C_6H_4-2-NO_2	91
7a	P^nBu_3	2	C_9H_6N	96
7b	P^nBu_3	2	C_6H_4-2-CHO	92
7c	P^nBu_3	2	C_6H_4-2-Cl	99
7d	P^nBu_3	2	C_6H_4-2-$C{\equiv}N$	90
7e	P^nBu_3	2	C_6H_4-2-NO_2	98
8a	$P(OMe)_3$	1	C_6H_4-2-CHO	84
8b	$P(OMe)_3$	1	C_6H_4-2-NO_2	70
9	$P(OMe)_3$	2	C_6H_4-2-NO_2	85
10	$P(OCH_2CF_3)_3$	1	C_6H_4-2-NO_2	93

[a] Based on silver(I) phenolates **3a–3e**.

3. Results and discussion

3.1. Syntheses und characterization of complexes **3–9**

As synthesis methodology for the preparation of phosphane and phosphite silver(I) phenolates $[L_mAgOR]$ (**6–10**) (Table 1) we decided to use as starting materials metal–organic [AgOR] (**3a**, R = C_9H_6N; [12a] **3b**, R = C_6H_4-2-CHO, **3c**, R = C_6H_4-2-Cl; **3d**, R = C_6H_4-2-$C{\equiv}N$; **3e** R = C_6H_4-2-NO_2 [12b]) which are accessible upon treatment of $[AgNO_3]$ (**1**) with equimolar amounts of the alcohols HOR (**2a**, R = C_9H_6N; **2b**, R = C_6H_4-2-CHO; **2c**, R = C_6H_4-2-Cl; **2d**, R = C_6H_4-2-$C{\equiv}N$; **2e**, R = C_6H_4-2-NO_2) in presence of NEt_3 (Eq. (1)). To obtain the desired silver(I) alcoholates in pure form it was advantageous to use as solvent acetonitrile-ethanol mixtures of ratio 1:20 and to carry out the reactions at 0 °C. Within the course of the reactions silver(I) phenolates **3a–3e** precipitated and hence, could easily be separated by decanting the supernatant solution. Complexes **3a–3e** were obtained as colorless to orange-red solids in yields between 16 and 88%. These complexes tend to decompose during minutes (**3b**, **3c**) or days (**3a**, **3d**, **3e**) to give unidentified products at ambient temperature. Thus, storage at −30 °C is advisable. In addition, **3a–3e** are sensitive to light and should best be maintained in the dark, otherwise decomposition to elemental silver occurs. Metal–organic **3e** is soluble without decomposition in water.

$$\underset{\mathbf{1}}{[AgNO_3]} + \underset{\mathbf{2}}{\text{H-OR}} \xrightarrow[\substack{CH_3CN\,/\,EtOH \\ -\,HNEt_3^+NO_3^-}]{NEt_3} \underset{\mathbf{3}}{[AgOR]}$$

A conventional synthesis route to the phosphane and phosphite silver(I) phenolates $[L_mAgOR]$ (L = P^nBu_3, *m* = 1: **6a**, R = C_9H_6N; **6b**, R = C_6H_4-2-CHO; **6c**, R = C_6H_4-2-Cl; **6d**, R = C_6H_4-2-$C{\equiv}N$; **6e**, R = C_6H_4-2-NO_2. *m* = 2: **7a**, R = C_9H_4; **7b**, R = C_6H_4-2-CHO; **7c**, R = C_6H_4-2-Cl; **7d**, R = C_6H_4-2-$C{\equiv}N$; **7e**, R = C_6H_4-2-NO_2. L = $P(OMe)_3$, *m* = 1: **8a**, R = C_6H_4-2-CHO; **8b**, R = C_6H_4-2-NO_2. *m* = 2: **9**, R = C_6H_4-2-NO_2. L = $P(OCH_2CF_3)_3$, *m* = 1: **10**, R = C_6H_4-2-NO_2) is given by reacting [AgOR] (**3a–3e**) with Lewis-bases L (**4**, L = P^nBu_3; **5a**, L = $P(OMe)_3$; **5b**, L = $P(OCH_2CF_3)_3$) in ratios of 1:1 (synthesis of **6**, **8**, **10**) or 1:2 (synthesis of **7** and **9**) in diethyl ether or dichloromethane solutions at 0 °C (Eq. (2), Table 1). After appropriate work-up, complexes **6–10** could be isolated as colorless to pale orange solids (**6** and **8–10**) or beige to red liquids (**7**) in excellent yield (Table 1, Section 2). They are somewhat light-sensitive and turn grey or brown on prolonged standing at ambient temperature. This differs from **3a–3e**, since these species decompose readily upon exposure to light at 25 °C (vide supra). While **3a–3e** are insoluble in most common organic solvents, metal–organic **6–10** dissolve in tetrahydrofuran, dichloromethane and diethyl ether.

$$\underset{\mathbf{3}}{[AgOR]} + \underset{\mathbf{4,\,5}}{m\,L} \xrightarrow{Et_2O \text{ or } CH_2Cl_2} \underset{\mathbf{6\,-\,10}}{[L_mAgOR]}$$

Complexes **3a–3e** have been characterized by IR and elemental analysis. For **6–10** additionally ^1H, $^{13}C\{^1H\}$ and $^{31}P\{^1H\}$ NMR spectroscopic studies, and for **7e** temperature-programmed and *in situ* molecular beam mass spectrometric experiments were carried out. For **8b** and **10** their molecular structures in the solid state were established.

The IR spectra of **3b**, **6b**, **7b** and **8a** are characterized by a distinct $\tilde{\nu}_{CO}$ vibration (aldehyde functionality) at ca. 1650 cm^{-1} (Experimental Part). The $\tilde{\nu}_{NO}$ absorption typical for **3e**, **6e**, **7e**, **8b**, **9** and **10** is observed at ca. 1500 cm^{-1}, while the $C{\equiv}N$ band for **3d**, **6d** and **7d** is found at 2209, 2207 and 2204 cm^{-1}, respectively.

The ^1H NMR spectra of **6–10** consist of well-resolved signals being in agreement with the expected resonance pattern for the organic phenolates, phosphanes and phosphites present (Section 2). The signal intensities confirm the composition of the appropriate complexes.

The most characteristic feature in the $^{13}C\{^1H\}$ NMR spectra of **6b**, **7b** and **8a** is the resonance signal for the aldehyde carbon atom at ca. 195 ppm. The $C{\equiv}N$ unit in **6d** and **7d** resonates at 113.9 and 110.9 ppm, respectively.

The $^{31}P\{^1H\}$ NMR spectra of **6–10** are of some more interest because they show that in solution ligand exchange processes occur (Section 2, Fig. 1). Similar observations were made for comparable phosphane silver(I) compounds, *i.e.* [(R_3P)Ag-β-diketonates] [15a] or [(R_3P)Ag-carboxylates] [15b]. For all phosphane and phosphite silver(I) phenolates two super-imposed doublets, with exception of **6b–6e**, are observed at low temperature ($^1J_{107Ag31P}$ and $^1J_{109Ag31P}$), due to coupling of the ^{31}P nucleus with the ^{107}Ag and ^{109}Ag isotopes having natural abundances of 52 and 48%, respectively (Section 2). [16] At 25 °C the $^{31}P\{^1H\}$ spectra are characterized by either broad doublets or broad singlets. Exemplary, the temperature-dependent $^{31}P\{^1H\}$ NMR spectra of **10** in the temperature range of 25 to −60 °C are shown in Fig. 1. This behavior corresponds to related silver(I) organic compounds, for a detailed discussion see reference [15b]. As it can be seen from Fig. 1 representative $^1J_{107Ag31P}$ and $^1J_{109Ag31P}$ coupling constants of 928 Hz and 1071 Hz are characteristic. Furthermore, it could be demonstrated that the exchange process becomes faster in the presence of an excess of phosphane or phosphite molecules [15].

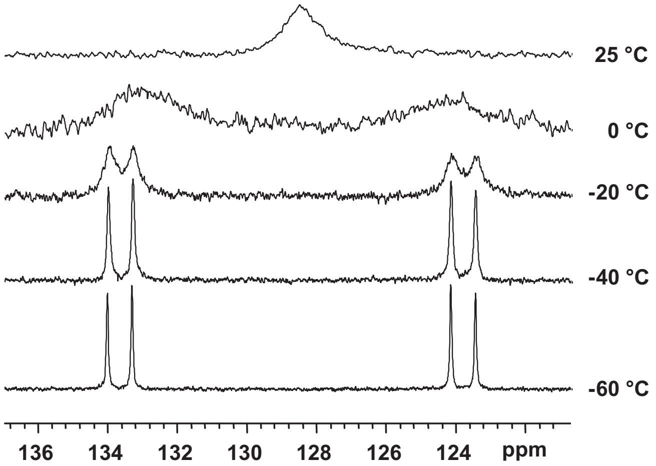

Fig. 1. Temperature-dependent $^{31}P\{^1H\}$ NMR spectra of **10** (in $CDCl_3$, temperature range 25 to −60 °C).

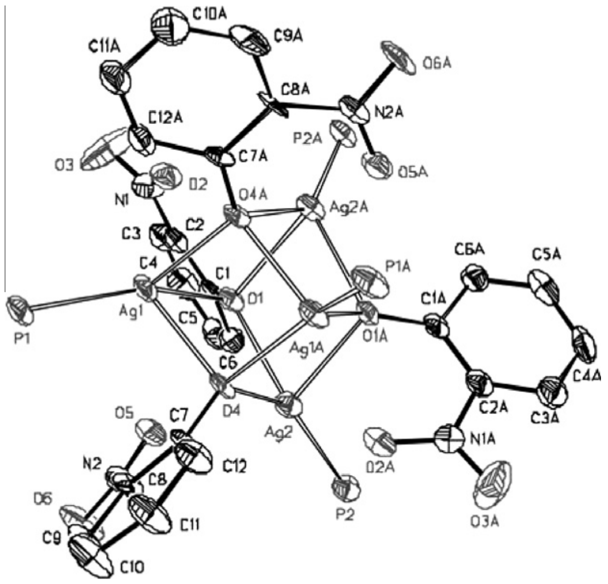

Fig. 2. ORTEP diagram (50% probability level) of **8b** with the atom numbering scheme. The hydrogen atoms, the OMe groups at phosphorus and the dichloromethane molecules as packing solvents are omitted for clarity. Symmetry transformations used to generate equivalent atoms are labeled with 'A': −x + 1, y, −z + 1/2.

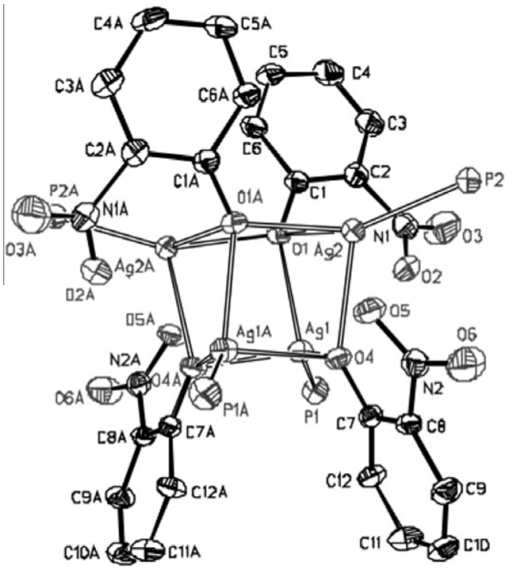

Fig. 3. ORTEP diagram (30% probability level) of **10** with the atom numbering scheme. The hydrogen atoms and the OCH_2CF_3 groups at phosphorus are omitted for clarity. Symmetry transformations used to generate equivalent atoms are labeled with 'A': −x, y, −z + 1/2.

Table 2
Selected distances (Å) and angles (°) for complexes **8b** and **10**[a].

	8b[b]	**10**[c]
Distances		
Ag1–P1	2.3244(19)	2.340(2)
Ag1–O4A	2.337(4)	2.567(6)
Ag1–O1	2.352(4)	2.411(5)
Ag1–O4	2.468(5)	2.298(5)
Ag2–P2	2.338(5)	2.290(6)
Ag2–O4	2.350(5)	2.343(2)
Ag2–O1	2.404(5)	2.411(5)
Ag2–O1A	2.459(4)	2.314(5)
Angles		
AgO_3P setup around Ag1		
P1–Ag1–O1	130.24(12)	121.00(15)
P1–Ag1–O4	115.67(12)	144.77(15)
P1–Ag1–O4A	143.00(12)	127.09(13)
O1–Ag1–O4	81.28(16)	87.82(18)
O1–Ag1–O4A	83.61(15)	83.08(17)
O4–Ag1–O4A	79.47(18)	71.8(2)
Ag_4O_4 interheterocuban		
Ag1–O1–Ag2	97.85(17)	90.04(17)
Ag1–O1–Ag2A	94.79(15)	95.13(18)
Ag1–O4–Ag2	96.13(16)	94.63(19)
Ag1–O4–Ag1A	100.42(18)	107.1(2)
AgO_3P setup around Ag2		
P2–Ag2–O1	132.59(12)	127.79(14)
P2–Ag2–O4	142.30(13)	120.19(14)
P2–Ag2–O1A	114.61(12)	144.08(15)
O1–Ag2–O4	82.70(16)	82.74(16)
O1–Ag2–O1A	78.26(16)	73.4(2)
O1A–Ag2–O4	81.05(15)	88.13(18)

[a] Standard deviations are given as the last significant figure(s) in parenthesis.
[b] Symmetry transformations used to generate equivalent atoms: −x + 1, y, −z + 1/2.
[c] Symmetry transformations used to generate equivalent atoms: −x, y, −z + 1/2.

The molecular structures of **8b** and **10** in the solid state were established by single X-ray structure analysis. Single crystals could be grown from slow diffusion of petroleum ether into a dichloromethane solution containing **8b** or **10** at −30 °C. A view of complexes **8b** and **10** is given in Figs. 2 and 3, respectively. Selected bond distances (Å) and angles (°) are summarized in Table 2. Crystal data and experimental details of **8b** and **10** are presented in Table 3.

Essentially, metal–organic **8b** and **10** are isostuctural crystallizing in the monoclinic space group *C2/c*. Both complexes possess a crystallographically imposed C_2 symmetry with the C_2 axis running through the centre of the Ag_2O_2 four-membered rings consisting of the atoms Ag2, O1, Ag2A, O1A and O4, Ag1, O4A, Ag1A for 8b, and Ag2, O1A, Ag2A, O1 and O4, Ag1A, O4A, Ag1 for **10**, respectively.

In both complexes the central Ag_4O_4 hetero-cubane unit, which is a most favoured structural motif for phosphane or phosphite Ag_4X_4 species (X = O, Br, I), [17–20] is set-up by the silver atoms Ag1, Ag2 and the symmetry generated atoms Ag1A and Ag2A as well as the corresponding oxygen atoms O1, O4, O1A and O4A (Figs. 1 and 2). The oxygen atoms are thereby acting as four electron donors and are -bridging three silver(I) ions. Each silver atom is additionally coordinated by one $P(OMe)_3$ (**8b**) or $P(OCH_2CF_3)_3$

Table 3
Crystal, intensity collection and refinement data for **8b** and **10**.

	8b	**10**
Empirical formula	$C_{38}H_{56}Ag_4Cl_4N_4O_{24}P_4$	$C_{12}H_{10}AgF_9NO_6P$
Formula weight [g mol^{-1}]	1650.03	574.05
Crystal system	monoclinic	monoclinic
Space group	*C*2/*c*	*C*2/*c*
a (Å)	22.717(7)	29.715(3)
b (Å)	11.979(4)	10.8345(10)
c (Å)	21.764(7)	27.175(3)
β (°)	104.196(6)	115.957(2)
V (Å^3)	5742(3)	7866.3(13)
Z	4	16
Crystal size (mm)	0.4 × 0.3 × 0.3	0.35 × 0.3 × 0.25
Density (calc.) (g cm^{-3})	1.909	1.939
θ Range for data collection /°	1.93–26.41	1.52–25.44
Completeness to θ (%)	97.4	97.2
R_{int}	0.0745	0.0595
F(0 0 0)	3280	4480
Temperature (K)	183(2)	298(2)
Reflections collected	16376	20693
Independent reflections	6018	7072
Parameter	358	771
Goof (*S*) based on F^2	1.027	1.040
Largest diff. peak and hole /e·Å^{-3}	2.652, −2.740	1.360, −0.922
Absorption coefficient [mm^{-1}]	1.722	1.219
R_1: $I \geq 2\sigma(I)$/all	0.0715, 0.0966	0.0715, 0.1134
wR_2: $I \geq 2\sigma(I)$/all	0.1756, 0.1943	0.1953, 0.2159

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

(**10**) ligand resulting in a somewhat distorted tetrahedral surrounding at silver. The Ag–O distances (2.29–2.47 Å) and P-Ag–O (71.9–71.8°) and O–Ag–O angles (104.8–144.1°) are in agreement with this structural motif [19,20]. Due to this, also different silver–phosphorus separations are observed (**8b**: Ag1–P1 2.3244(19), Ag2–P2 2.338(5) Å; **10**: Ag1–P1 2.340(3), Ag2–P2 2.290(6) Å) (Figs. 1 and 2). In both complexes the *ortho*-positioned NO_2 group is free (Figs. 1 and 2).

3.2. Thermogravimetric studies

TG studies (= thermogravimetry) were carried out to obtain first informations on the decomposition temperature and on the relative stability of the respective phosphane and phosphite silver(I) alcoholates. The TG traces show one- or two-step decompositions (Section 2). Exemplary, the TG traces of **7a** and **7e** are depicted in Fig. 4. Both complexes merely display an overall decomposition starting at 100 (**7a**) or 120 °C (**7e**) and ending at 276 (**7e**) or 350 °C (**7a**). The mass loss of 83.2% (**7a**) and 69.5% (**7e**) is in accordance with the theoretical percentage calculated for the formation of elemental silver from **7a** and **7b**, respectively.

3.3. Temperature-dependent and in situ molecular beam mass spectrometric studies

Temperature-programmed mass spectrometry is a general method to determine the volatility and thermal stability of molecules. It has been shown that **7e** is volatile but temperature-instable during the evaporation process, as different fragments representing **7e** can be found in different temperature intervals. [11] Between 230–310 °C and 340–380 °C, phosphane fragments have been identified at *m*/*z* = 202 [$C_4H_9P^+$] and *m*/*z* = 76 [$C_3H_9P^+$] and a nitrophenol fragment at *m*/*z* = 139 [$C_6H_5NO_3^+$]. A silver-containing ion (*m*/*z* = 309 [$C_{12}H_{27}Pg^+$]) has been detected in the temperature range of 230–310 °C. Additionally, investigations under typical CVD conditions were analyzed using *in situ* molecular beam mass spectrometry. An evaporation temperature of 190 °C has been chosen in accord with the TG experiment of **7e** (Fig. 4). This temperature is slightly below the main decomposition interval and hence, silver-containing fragments could be detected at this temperature. In Fig. 5 the signal intensities of selected fragments in dependence of the deposition temperature are shown. Only at a deposition temperature of 190 °C, a silver-containing fragment at *m*/*z* = 511 [$(C_4H_9P)_2Ag]^+$ is observed. At deposition temperatures, the precursor decomposition in the gas phase is dominant as only fragments from the phosphane ligand (*m*/*z* = 202, [$C_4H_9P]^+$) and the nitrophenol group (*m*/*z* = 139 [$C_6H_5NO_3]^+$) can be detected with increasing intensity. From these data it can be concluded that **7e** can be considered as a promising CVD precursor candidate. Compared with, for example, [$(^nBu_3P)_2AgO_2CCH_2Ph$] a somewhat different fragmentation was observed [11], *e.g.* [$(Bu_3P)Ag]^+$ (*m*/*z* = 309), [$Bu_3P]^+$ (*m*/*z* = 202), and [$O_2CCH_2Ph]^+$ (*m*/*z* = 91, *m*/*z* = 136) were formed, while for **7e** ions such as [$(Bu_3P)_2Ag]^+$ and [$C_6H_5NO_3]^+$ are characteristic.

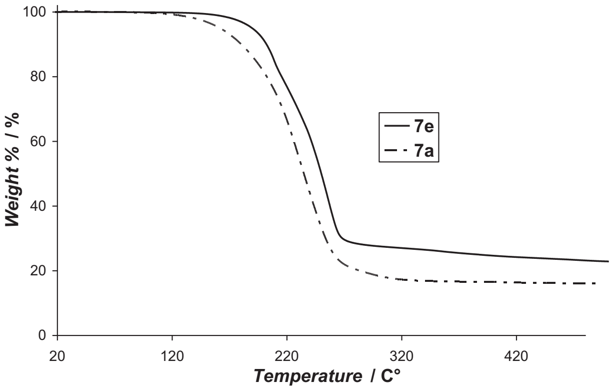

Fig. 4. TG trace of **7a** (Δm = 83.2%) and **7e** (Δm = 69.5%) (heating rate 8 K min^{-1}, nitrogen atmosphere (20 dm^3 h^{-1})).

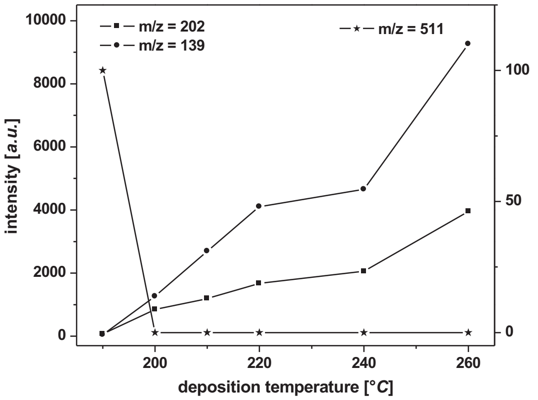

Fig. 5. *In situ* mass spectrometry: dependence of intensities on the deposition temperature for detected fragments from **7e** (*m*/*z* = 511 corresponds to [$(C_4H_9P)_2Ag]^+$, *m*/*z* = 202 to [$C_4H_9P]^+$, and *m*/*z* = 139 to [$C_6H_5NO_3]^+$).

3.4. Chemical vapor deposition studies

Based on the thermal properties (TGA) we chose **7e** as potential CVD precursor. The CVD experiments were performed in a vertical cold-wall CVD reactor with stagnation point flow geometry with a pulsed spray evaporation system. The precursor was evaporated at 190 °C and transported to the deposition zone by a heated quartz tube with 100 mm length at a pressure of 50 mbar. Argon was used as carrier gas at a flow rate of 100 sccm. As substrate pre-cleaned

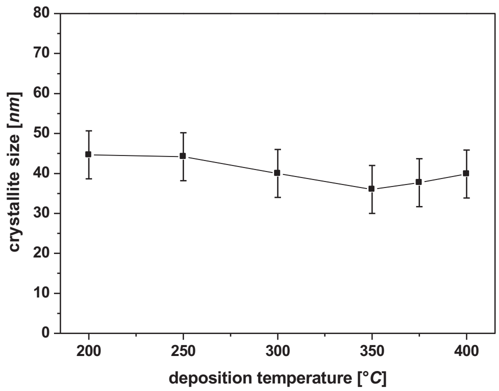

Fig. 6. Crystallite size vs. deposition temperature for depositions using metal–organic **7e**.

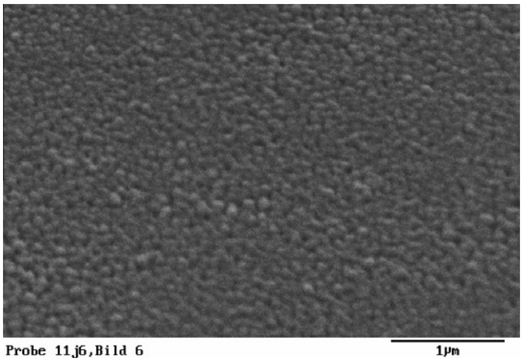

Fig. 7. SEM image of a film deposited at 5 mbar from **7e** at 350 °C, thickness 200 nm.

(hot sulfuric acid, acetone, and ethanol in an ultrasonic bath) glass (square, diameter 25 mm) was applied; deposition experiments were carried out in the temperature interval of 200–400 °C. The films were analyzed using XRD (= X-ray Diffraction) and SEM (= Scanning Electron Microscopy). Only the stable cubic crystalline structure of silver was observed for all films represented by reflections at $2\Theta = 38.11$ (1 1 1) (predominant), $2\Theta = 44.28$ (2 0 0), $2\Theta = 64.42$ (2 2 0), and $2\Theta = 77.47°$ (3 1 1). The crystallite size was calculated with a crystallite size of ca. 40 nm using the Scherrer equation (Fig. 6).

As it can be seen from Fig. 7 the morphology of the obtained silver film grown at 350 °C is homogeneous and dense. The grain size of 40 nm is typical for silver films deposited under these conditions. [11]

EDX (= Energy Dispersive X-ray Spectroscopy) investigations evinced that carbon as only impurity could be located on the surface of the silver film.

4. Conclusion

Silver(I) phenolates [AgOR] (R = C_9H_6N, C_6H_4-2-CHO, C_6H_4-2-Cl, C_6H_4-2-C≡N, C_6H_4-2-NO_2), which are accessible by the stoichiometric reaction of [$AgNO_3$] with HOR (C_9H_6N, C_6H_4-2-CHO, C_6H_4-2-Cl, C_6H_4-2-C≡N, C_6H_4-2-NO_2) in presence of NEt_3, can successfully be applied in the synthesis of the phosphane and phosphite silver(I) phenolates [L_mAgOR] (*m* = 1, L = P^nBu_3, R = C_9H_6N; R = C_6H_4-2-CHO; R = C_6H_4-2-Cl; R = C_6H_4-2-C≡N; R = C_6H_4-2-NO_2. *m* = 2, L = P^nBu_3, R = C_9H_4; R = C_6H_4-2-CHO; R = C_6H_4-2-Cl; R = C_6H_4-2-C≡N; R = C_6H_4-2-NO_2. *m* = 1, L = $P(OMe)_3$, R = C_6H_4-2-CHO; R = C_6H_4-2-NO_2. *m* = 1, L = $P(OCH_2CF_3)_3$, R = C_6H_4-2-NO_2. *m* = 2, L = $P(OMe)_3$, R = C_6H_4-2-NO_2) by treatment of [AgOR] with P^nBu_3, $P(OMe)_3$ or $P(OCH_2CF_3)_3$ in the ratios of 1:1 or 1:2. The molecular solid state structure of [$(MeO)_3PAgOC_6H_4$-2-NO_2] and [$(CF_3CH_2)_3PAgOC_6H_4$-2-NO_2] was determined. These metal–organic compounds are isostructural and possess a hetero-cubane Ag_4O_4 core. Low-temperature $^{31}P\{^1H\}$ NMR studies show that the appropriate phosphane and phosphite complexes are dynamic in solution and rapidly exchange at room temperature their ligands. Based on TG, temperature-programmed and *in situ* molecular beam mass spectrometry, compound [$(^nBu_3P)_2AgOC_6H_4$-2-NO_2] was chosen as CVD (= Chemical Vapor Deposition) precursor in the deposition of silver onto glass substrates. The resulting silver films were characterized by XRD. The SEM image of a film grown at 350 °C shows a homogeneous and dense surface with grain sizes of 40 nm.

5. Supplementary material

CCDC 763980 and 763981 contain the supplementary crystallographic data for complexes **8b** and **10**, respectively. 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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