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Synthesis and characterization of organophosphine/phosphite stabilized *N*-silver(I) succinimide: crystal structure of $[(Ph_3P)_3 \cdot AgNC_4H_4O_2]$

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ABSTRACT

Six organophosphine/phosphite stabilized *N*-silver(I) succinimide complexes of the type $L_n \cdot AgNC_4H_4O_2$ ($L = PPh_3$; $n = 1$, **2a**; $n = 2$, **2b**; $n = 3$, **2c**; $L = P(OEt)_3$; $n = 1$, **2d**; $n = 2$, **2e**; $n = 3$, **2f**) have been prepared by reacting $[AgNC_4H_4O_2]$, which can be synthesized from succinimide and excessive Ag_2O in boiling water, with triphenylphosphine or triethylphosphite in dichloromethane under a nitrogen atmosphere. These complexes were obtained in high yields and characterized by elemental analysis, ^1H, $^{13}C\{H\}$ NMR, IR spectroscopy and thermal analysis (TG and DSC). The molecular structure of **2c** has been determined by X-ray single crystal analysis, in which the silver atom is in a distorted tetrahedral geometry.

1. Introduction

Silver(I) complexes have been widely studied due to their rich structural information [1–6], potential applications in catalysis [7] and material science [8,9]. Recently renewed interest has been paid to Lewis-base stabilized silver(I) complexes, mostly because of their application as precursors in the growth of silver thin films via chemical vapor deposition (CVD) techniques, which could be used as an interconnector for future generation of deep submicron integrated circuits due to lower resistivity and superior electromigration resistance [10].

OrganoMetallic Chemical Vapor Deposition (OMCVD) is a very effective technique for the growth of high quality metal films, because of its high deposition rates with good step coverage [11–14] and the high aspect ratio in the multilevel metallization structure [15]. Precursors for CVD should have: (i) good volatility during the evaporation and transportation in the gas phase; (ii) high purity and a suitable thermal decomposition mechanism; (iii) suitable thermal stability which means that it cannot decompose during the transportation but will decompose easily in the CVD reactor [16,17]. Out of this, the development of a new generation of silver(I) complexes as precursors has had an enormous impact. The silver precursors most often used in CVD are organometallic or β-diketonate complexes with tertiary phosphines (PMe_3, PEt_3) [18,19], alkenes or [20] alkynes [21,22] as ancillary ligands and Lewis-base stabilized silver(I) carboxylates [23–30]. Of the latter ones, volatile perfluorinated and aliphatic Ag(I) carboxylates and their complexes with tertiary phosphines have been reported [23–28]. The experiment shows that the organophosphine stabilized silver(I) carboxylates were thermally stable, and decomposed to silver over a wide temperature range and with an interesting decomposition mechanism [29]. The properties of silver(I) complexes having Ag–O [24–26,30–32], Ag–X [21,25] or Ag–C [21,28] bonds have been investigated frequently, whilst silver(I) complexes having Ag–N bonds have rarely been reported. To the best of our knowledge, Lewis-base stabilized *N*-silver(I) succinimide complexes have not been reported. In order to search for a new kind of silver complex to be used as a precursor for the CVD technique, herein we describe the synthesis and characterization of a series of organophosphine/phosphite stabilized *N*-silver(I) succinimide complexes, $[L_n \cdot AgNC_4H_4O_2]$ ($L = PPh_3$, $n = 1$, **2a**; $n = 2$, **2b**; $n = 3$, **2c**; $L = P(OEt)_3$; $n = 1$, **2d**; $n = 2$, **2e**; $n = 3$, **2f**). The single crystal structure of **2c** has been determined and is discussed as well in this paper.

2. Experimental

2.1. General procedures

All operations were carried out under an atmosphere of purified nitrogen with standard Schlenk techniques. The solvent dichloromethane (CH_2Cl_2) was purified by distillation from P_2O_5 under N_2 before use. The *N*-silver(I) succinimide was synthesized by succinimide with excessive Ag_2O in boiling water. ^1H NMR were recorded on a Bruker Avance 300 spectrometer operating at 300.130 MHz in the Fourier transform mode; $^{13}C\{H\}$ NMR spectra were recorded at 75.467 MHz. Chemical shifts are reported in δ units (parts per million) downfield from tetramethylsilane ($\delta = 0.0$ ppm) with the solvent as the reference signal (^1H NMR, $CDCl_3$ $\delta = 7.26$; $^{13}C\{H\}$ NMR,

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$CDCl_3$ δ = 77.55). Infrared spectra were collected on Bruker Vector 22 in KBr at room temperature. Elemental analysis was performed on a Perkin–Elmer 240 C elemental analyzer. ThermoGravimetric (TG) and Differential Scanning Calorimetric (DSC) studies were carried out with a NETZSCH STA 449 C with a constant heating rate of 10 °C min^{-1} under Argon (1.0 cm^3 min^{-1}). Melting points were observed in sealed capillaries and are uncorrected.

2.2. Synthesis

2.2.1. Synthesis of $AgNC_4H_4O_2$ (**1**)

Silver oxide (5.0 g, 22 mmol) was added in one portion to a boiling solution of succinimide (3.8 g, 38 mmol) in 100 ml water. The reaction vessel was wrapped with aluminum foil in order to exclude as much light as possible. After the stirred solution was heated to reflux for 45 min and the silver oxide disappeared, the suspension was filtered through a heated Büchner funnel into a filter flask, also wrapped with aluminum foil. The filtrate was allowed to stand at room temperature overnight, during which time *N*-silver(I) succinimide crystallized. The *N*-silver(I) succinimide was separated on a Büchner funnel, dried in a vacuum oven for 1 h at 110 °C. The product was stored under nitrogen and kept in dark place. Yield: 3.1 g (40%, based on Ag_2O) [33].

2.2.2. Synthesis of $Ph_3P \cdot AgNC_4H_4O_2$ (**2a**)

Triphenylphosphine (0.1318 g, 0.5 mmol) dissolved in 20 mL of CH_2Cl_2 was added dropwise into a stirred solution of *N*-silver(I) succinimide (0.1029 g, 0.5 mmol) suspended in 20 mL of CH_2Cl_2 at 0 °C. A clear solution was obtained by filtration through a pad of celite after stirring the reaction mixture for 6 h at 0 °C. A white solid product was obtained after removing all the volatiles with an oil-pump vacuum, yield: 0.22 g (94% based on *N*-silver(I) succinimide). Mp.: 182–183 °C dec. *Anal. Calc.* for $C_{22}H_{19}O_2AgPN$: C, 56.43; H, 4.09. Found: C, 56.36; H, 4.04%. ^1H NMR ($CDCl_3$): δ 2.7 (s, 4 H, CH_2–H), 7.4–7.6 (m, 15 H, Ph-H). $^{13}C\{H\}$ NMR ($CDCl_3$): δ 32.1 (CH_2), δ 191.4 (C), 134.0 (J_{PC} = 16.0 Hz, C_6H_5), 131.3 (C_6H_5), 129.9 (C_6H_5), 129.2 (J_{PC} = 10.9 Hz, C_6H_5). IR (KBr) data (cm^{-1}): 3049 (m), 2963 (m), 1709 (m), 1611 (s), 1436 (s), 1348 (s), 1282 (s), 1157 (m), 1096 (s), 1026 (m), 806 (m), 745 (s), 693 (s), 507 (s), 451 (m).

2.2.3. Synthesis of $(Ph_3P)_2 \cdot AgNC_4H_4O_2$ (**2b**)

Complex **2b** was obtained by following the above procedure, only using *N*-silver(I) succinimide (0.1379 g, 0.67 mmol) and triphenylphosphine (0.3515 g, 1.34 mmol) instead. Yield: 0.47 g (96% based on *N*-silver(I) succinimide). Mp.: 196–197 °C. *Anal. Calc.* for $C_{40}H_{34}O_2AgP_2N$: C, 65.77; H, 4.69. Found: C, 65.63; H, 4.63%. ^1H NMR ($CDCl_3$): δ 2.6 (s, 4 H, CH_2–H), 7.3–7.5 (m, 30 H, Ph-H). $^{13}C\{H\}$ NMR ($CDCl_3$): δ 32.5 (CH_2), δ 192.4 (C), 133.9 (J_{PC} = 16.8 Hz, C_6H_5), 132.6 (J_{PC} = 24.1 Hz, C_6H_5), 130.0 (C_6H_5), 128.7 (J_{PC} = 9.5 Hz, C_6H_5). IR (KBr) data (cm^{-1}): 3655 (m), 3049 (m), 2962 (m), 2361 (w), 1700 (m), 1603 (s), 1583 (m), 1478 (m), 1434 (s), 1345 (s), 1285 (s), 1247 (s), 1183 (w), 1095 (s), 1026 (m), 996 (m), 803 (m), 746 (s), 695 (s), 512 (s), 436 (m).

2.2.4. Synthesis of $(Ph_3P)_3 \cdot AgNC_4H_4O_2$ (**2c**)

Complex **2c** can be synthesized in the same manner as **2a** (Section 2.2.2). In this respect, triphenylphosphine (0.4328 g, 1.65 mmol) was reacted with *N*-silver(I) succinimide (0.1132 g, 0.55 mmol). After appropriate work-up (see Section 2.2.1), complex **2c** was obtained as a white solid. Yield: 0.51 g (93% base on *N*-silver(I) succinimide). Mp.: 194–196 °C dec. *Anal. Calc.* for $C_{58}H_{49}AgO_2P_3N$: C, 70.17; H, 4.98. Found: C, 69.91; H, 4.73%. ^1H NMR ($CDCl_3$): δ 2.5 (s, 4 H, CH_2–H), 7.3–7.5 (m, 45 H, Ph-H). $^{13}C\{H\}$ NMR ($CDCl_3$): δ 32.5 (CH_2), δ 192.5 (C), 134.0 (J_{PC} = 4.8 Hz, C_6H_5), 133.8 (J_{PC} = 8.6 Hz, C_6H_5), 129.6 (C_6H_5), 128.6 (J_{PC} = 8.8 Hz, C_6H_5). IR (KBr) data (cm^{-1}): 3047 (m), 1703 (m), 1598 (s), 1477 (m), 1434 (s), 1344 (s), 1282 (s), 1245 (s), 1157 (m), 1096 (s), 1026 (m), 998 (m), 806 (m), 743 (s), 694 (s), 513 (s), 465 (m).

2.2.5. Synthesis of $(EtO)_3P \cdot AgNC_4H_4O_2$ (**2d**)

Complex **2d** can be synthesized by a similar procedure used for the synthesis of **2a** (Section 2.2.1). In this respect, $[(EtO)_3P]$ (1.87 g, 11.27 mmol) was reacted with *N*-silver(I) succinimide (2.32 g, 11.27 mmol). After appropriate work-up, complex **2d** was isolated as a white solid. Yield: 3.81 g (91% based on *N*-silver(I) succinimide). Mp.: 53–54 °C. *Anal. Calc.* for $C_{10}H_{19}O_5AgPN$: C, 32.28; H, 5.15. Found: C, 32.16; H, 5.02%. ^1H NMR ($CDCl_3$): δ 1.3 (t, 9H, CH_3/CH_3CH_2–, J_{HH} = 7.0 Hz), δ 2.6 (s, 4H, CH_2–H), 4.0 (m, 6 H, CH_2/CH_3CH_2–). $^{13}C\{H\}$ NMR ($CDCl_3$): δ 31.9 (CH_2), δ 191.0 (C), 16.1 (J_{PC} = 6.7 Hz, CH_3/CH_3CH_2–), 61.3 (J_{PC} = 3.8 Hz, CH_2/CH_3CH_2–). IR (KBr) data (cm^{-1}): 3437 (m), 2981 (m), 2926 (m), 1701 (m), 1613 (s), 1441 (m), 1358 (s), 1296 (s), 1248 (s), 1163 (s), 1021 (s), 935 (s), 774, (s), 669 (s), 535 (s), 475 (m).

2.2.6. Synthesis of $[(EtO)_3P]_2 \cdot AgNC_4H_4O_2$ (**2e**)

Complex **2e** can be synthesized in the same manner as **2a** (Section 2.2.2). In this respect, $[(EtO)_3P]$ (1.4044 g, 8.46 mmol) was reacted with *N*-silver(I) succinimide (0.8708 g, 4.23 mmol). After appropriate work-up (see Section 2.2.1) complex **2e** was obtained as a colorless liquid. Yield: 2.09 g (92% based on *N*-silver(I) succinimide). *Anal. Calc.* for $C_{16}H_{34}O_8AgNP_2$: C, 35.70; H, 6.37. Found: C, 35.57; H, 6.38. ^1H NMR ($CDCl_3$): δ 1.2 (t, 18 H, CH_3/CH_3CH_2–, J_{HH} = 7.0 Hz), δ 2.5 (s, 4 H, CH_2–H), 3.9 (m, 12 H, CH_2/CH_3CH_2–). $^{13}C\{H\}$ NMR ($CDCl_3$): δ 31.8 (CH_2), δ 191.0 (C), 16.1 (J_{PC} = 6.1 Hz, CH_3/CH_3CH_2–), 60.0 (J_{PC} = 5.7 Hz, CH_2/CH_3CH_2–). IR (KBr) data (cm^{-1}): 3440 (m), 2979 (s), 2934 (m), 2901 (m), 2358 (w), 1715 (m), 1612 (s), 1477 (m), 1441 (m), 1391 (s), 1348 (s), 1287 (s), 1245 (s), 1162 (m), 1097 (m), 1022 (s), 937 (s), 771 (s), 669 (m), 536 (s), 442 (m).

2.2.7. Synthesis of $[(EtO)_3P]_3 \cdot AgNC_4H_4O_2$ (**2f**)

Complex **2f** was synthesized in a similar procedure to that used for the synthesis of **2a** (Section 2.2.1). In this respect, $[(EtO)_3P]$ (1.5538 g, 9.36 mmol) was reacted with *N*-silver(I) succinimide (0.6423 g, 3.12 mmol). After appropriate work-up, complex **2d** was isolated as a colorless liquid. Yield: 2.03 g (92% based on *N*-silver(I) succinimide). *Anal. Calc.* for $C_{22}H_{49}O_{11}AgP_3N$: C, 37.51; H, 7.01. Found: C, 37.32; H, 6.89%. ^1H NMR ($CDCl_3$): δ 1.3 (t, 27H, CH_3/CH_3CH_2–, J_{HH} = 7.0 Hz), δ 2.6 (s, 4 H, CH_2–H), 4.0 (m, 18 H, CH_2/CH_3CH_2–). $^{13}C\{H\}$ NMR ($CDCl_3$): δ 32.1 (CH_2), δ 191.5 (C), 16.2 (J_{PC} = 5.9 Hz, CH_3/CH_3CH_2–), 59.5 (J_{PC} = 6.6 Hz, CH_2/CH_3CH_2–). IR (KBr) data (cm^{-1}): 3414 (m), 2979 (s), 2926 (m), 2898 (m), 1701 (m), 1598 (s), 1437 (m), 1441 (w), 1391 (m), 1348 (s), 1295 (s), 1252 (s), 1162 (m), 1097 (m), 1023 (s), 933 (s), 773, (s), 669 (m), 556 (m), 454 (m).

2.3. Single crystal structure of $(Ph_3P)_3 \cdot AgNC_4H_4O_2$ (**2c**)

Single crystals of **2c** could be obtained by cooling a saturated dichloromethane solution to −20 °C. Suitable crystals for X-ray determination were placed in glue under N_2 due to their sensitive nature to oxygen and moisture. The X-ray structure measurement was performed on a BRUKER SMART Apex CCD, detector equipped with graphite monochromatic Mo Kα radiation (λ = 0.71073 Å), at room temperature. The program SMART [34] was used for determination of the unit cell. Data reduction and integration was carried out with SAINT [34] and absorption corrections were applied using the program SADABS [35]. The structure was solved using direct methods and refined by full-matrix least-squares procedures on

Table 1
Crystallographic data and analysis parameters for $(Ph_3P)_3 \cdot AgNC_4H_4O_2 \cdot 3CH_2Cl_2$.

Formula	$C_{58}H_{49}AgNO_2P_3 \cdot 3(CH_2Cl_2)$
Formula weight	1247.54
Space group	$P\bar{1}$
Crystal size (mm)	0.6 × 0.5 × 0.4
Crystal system	triclinic
Z value	2
a (Å)	13.070(3)
b (Å)	13.496(3)
c (Å)	20.073(4)
α (°)	94.283(4)
β (°)	105.502(4)
γ (°)	116.693(3)
D_{calc} [g/cm^3]	1.395
Index ranges	$-15 \leqslant h \leqslant 15$, $-16 \leqslant k \leqslant 10$, $-23 \leqslant l \leqslant 20$
Crystal shape/color	block/colorless
$F(000)$	1276
μ (Mo Kα) (mm^{-1})	0.73
λ (Mo Kα) (Å)	0.71073
Temperature (K)	295(2)
θ Range (°)	1.9–25.0
Independent reflections $[(I) > 2\sigma(I)]$	10274
R_1 $[I > 2\sigma(\theta)]$[a]	0.066
wR_2 $[I>2\sigma(\theta)]$[b]	0.160
Goodness-of-fit (GOF) on F^{2}[c]	1.18
$\Delta\rho_{max}$ (e Å^{-3})	1.10
$\Delta\rho_{min}$ (e Å^{-3})	−0.78

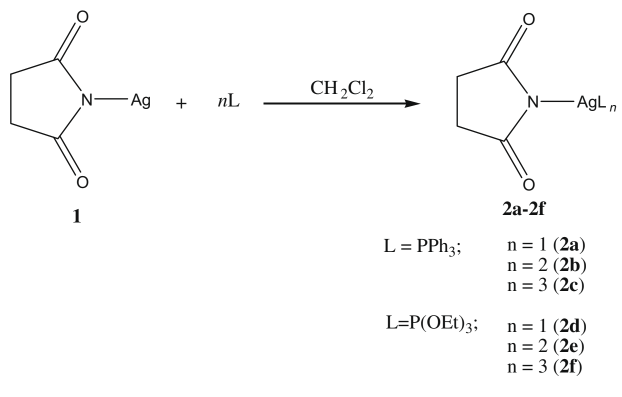
[a] $R_1 = \sum(||F_o| - |F_c||)/\sum|F_o|$; $wR_2 = [\sum(w(F_o^2 - F_c^2)^2)/\sum(wF_o^4)]^{1/2}$.
[b] $w = 1/[\sigma^2(F_o^2) + (0.064P)^2]$, $P = (F_o^2 + 2F_c^2)/3$.
[c] $S = [\sum w(F_o^2 - F_c^2)^2]/(n - p)^{1/2}$, n = number of reflections, p = parameters used.

F^2 (SHELX-97) [36]. All of the non-hydrogen atoms were refined with anisotropic displacement parameters. Crystallographic data and details on refinement are presented in Table 1. The crystal structure of **2c** is drawn using ORTEP [37].

3. Results and discussion

3.1. Synthesis

The phosphine/phosphite stabilized *N*-silver(I) succinimide complexes of the type $[L_n \cdot AgNC_4H_4O_2]$ (L = PPh_3, n = 1, **2a**; n = 2, **2b**; n = 3, **2c**; L = $P(OEt)_3$; n = 1, **2d**; n = 2, **2e**; n = 3, **2f**) were prepared by reacting $Ph_3P/(EtO)_3P$ with *N*-silver(I) succinimide in dichloromethane in stoichiometric amounts at 0 °C in high yield (Scheme 1). The complexes were isolated as white solids (**2a**–**2c**) or colorless liquids (**2d**–**2f**). They are very sensitive to moisture, oxygen as well as light. The complexes are insoluble in cold nonpolar solvents such as petroleum, whereas they are highly soluble in polar or unsaturated hydrocarbons such as methylenechloride, benzene and tetrahydrofuran. All the products obtained gave satisfactory elemental analysis results and were characterized by FT-IR, ^{1}H NMR and ^{13}C {H} NMR spectroscopy.



Scheme 1. Synthesis of complexes **2a**–**2f**.

The spectra of succinimide were investigated by Woldbaek, Klaeboe and Christensen [38]. Assignments are proposed by comparison with the normal-coordinate interpretation presented by the authors mentioned above. So far, discussion of the IR spectra of the metal complexes has been restricted to the stretching carbonyl band (1700 cm^{-1}) [39].

In the IR spectra, the broad N–H stretching band (∼3170 cm^{-1}) in succinimide disappears in the complexes obtained, as well as the sharp band at 820 cm^{-1} assigned to the out-of-plane N–H bending mode [38]. The in-plane N–H bending vibration has been tentatively associated with a sharp peak at 1418 cm^{-1} in succinimide, with an overtone at ∼2800 cm^{-1}. The overtone is absent from the spectra of the complexes. This illustrates the formation of a Ag–N bond.

In the 1600–1800 cm^{-1} region, succinimide contains sharp peaks at 1773 and 1695 cm^{-1} for the in-phase and out-of-phase stretching motions of the C═O groups [38]. In the *N*-silver(I) succinimide complexes, these bands are found at 1700–1710 and 1580–1615 cm^{-1}, respectively. These changes, which are correlated with those found for the uracil moiety [38], could be ascribed to the delocalization of the anionic charge to the ring and carbonyl groups, thus decreasing the C═O bond order (Scheme 2). The (C═O) region is very sensitive to proton substitution, but rather insensitive to whether the C═O groups are involved in metal coordination [38]. A weak band at 420 cm^{-1}, believed to involve the C═O in-plane bending vibration, was shifted to 436–475 cm^{-1} in the complexes. However, the weakness of these bands in the infrared spectra complicates their use for diagnostic purposes.

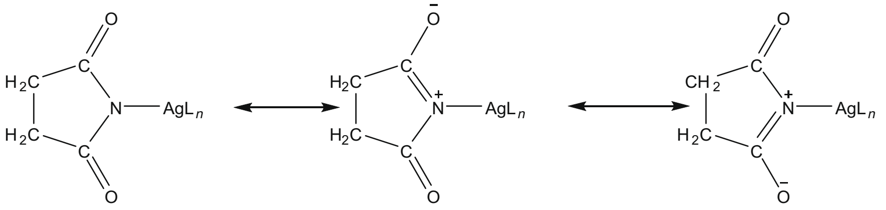
The NMR spectra (^{1}H and ^{13}C{H}) were recorded for all six complexes (see Section 2) at room temperature, The ^{1}H NMR spectra are consistent with the stoichiometries of the complexes. The protons of complexes **2a**–**2c** in the aryl proton region were in the range 7.2–7.6 ppm. The complexes (**2d**–**2f**) are easily distinguished because the resonances of the protons show only two groups. The proton of $–CH_2–$ in $C_4H_4NO_2–$ appeared at 2.5–2.7 ppm, which agrees well with that previously reported [40]. In the ^{13}C{H} NMR spectra, the triphenylphosphine carbon resonances of **2a**–**2c** are easily distinguished (128.6–134.1 ppm) from the resonance of $–CH_2–$ on $C_4H_4NO_2–$ (31.8–32.1 ppm).

3.2. Single crystal structure of **2c**

Single crystals of $[(Ph_3P)_3 \cdot AgNC_4H_4O_2]$ (**2c**) could be grown by slowly cooling a saturated dichloromethane solution containing **2c** to −20 °C. The molecular structure of **2c** is depicted in Fig. 1. Selected bond distances (Å) and bond angles (°) are given in Table 2.

Complex **2c** crystallizes in the triclinic space group $P\bar{1}$, and is composed of one molecule of $[(Ph_3P)_3 \cdot AgNC_4H_4O_2]$ and three molecules of dichloromethane (Fig. 1). In the complex, a four-coordinated silver(I) ion is present with three PPh_3 ligands occupying three of the coordination sites (PPP) and the nitrogen atom of succinimide occupying the fourth site, forming a distorted tetrahedral geometry around silver. The N–Ag–P(1) (107.29(1)°) and N–Ag–P(3) (94.95(1)°) angles are smaller than that of the ideal tetrahedral angle, while the P(1)–Ag–P(2) (113.70(5)°) and P(2)–Ag–P(3) (113.32(5)°) angles are larger (Table 2).

The succinimide ring is roughly planar; the N atom is 0.027 Å above the C(55)–C(56)–C(57)–C(58) plane, producing a slight "envelope" distortion in the ring. The succinimide ring is similar to the reported complex $[Li(Ag(Suc)_2) \cdot H_2O]$ [38]. The carbonyl oxygen, however, show different distances to the plane, implying the no coordinating interactions with silver.



Scheme 2. Delocalization of the anionic charge into the ring and carbonyl groups, decreasing the C=O bond order.

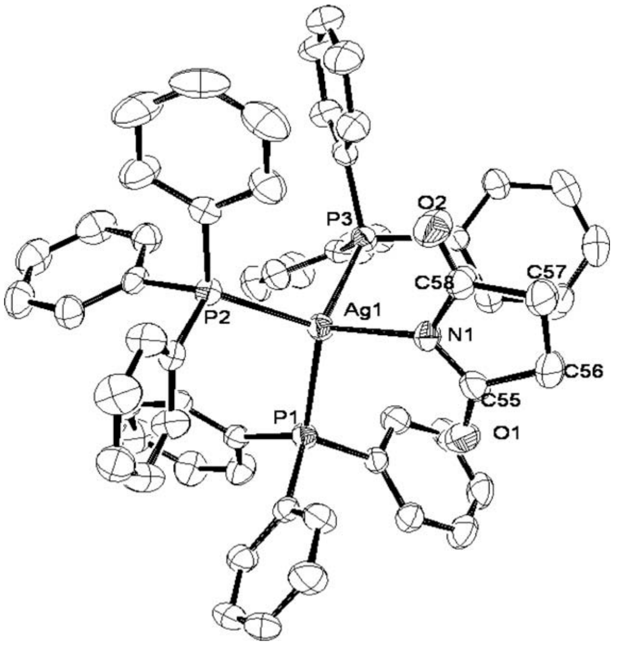


Fig. 1. ORTEP drawing of **2c**, showing 30% probability displacement ellipsoids. The hydrogen atoms and solvent molecules are omitted for clarity.

The C–N–C and N–C–C angles, depending on the substituent on nitrogen, are roughly correlated with the electrophilic character of the substituent. For instance, the C–N–C angle progressively decreases with decreasing substituent electrophilic character (115.0(15)°, C1; 111.6(7)°, Br; 112.6(6)°, H; 109.6(5)°, Ag; 108.3(4)°, Ni), whereas the adjacent N–C–C angles increase, but to a lesser extent (106.5(15)°, C1; 107.4(8)°, Br; 108.3(6)°, H; 111.9(6)°, Ag; 112.1(5)°, Ni) [38].

The Ag–P distances [2.619(2), 2.561(1), 2.575(2) Å] are longer than the sum of covalent radii of the P and Ag atoms (2.44 Å) [40] and that of [$(R_3P)_2$AgPI] (PI = $C_8H_4NO_2$) [2.4944(7) Å] [41]. The Ag–N distance [2.313(4) Å] is much longer than that of [$(R_3P)_2$AgPI] (PI = $C_8H_4NO_2$) [2.223(3) Å] [41] and the angles of P–Ag–P [113.70(5)° and 109.46(5)°] are much smaller than that of [$(Ph_3P)_2$AgPAZ] [130.88(5)° and 125.49(8)°] (PAZ = $C_8H_5N_2O$) [41].

3.3. Thermal analysis

The complex was studied by ThemoGravimetry (TG) to obtain information on transition, decomposition temperatures and frequencies and then by Differential Scanning Calorimetry (DSC) to determine the change of entropy during thermolysis. These studies are also required to optimize the temperature at which the respective single silver precursor should be maintained during the CVD experiments. For an example, the TG and DSC curves of complex **2d** are shown in Fig. 2. It can be seen from the DSC curve that there is one apparent endothermic process with a peak temperature of 55 °C, which could be attributed to the melting process of complex

Table 2
Selected bond lengths (Å) and bond angles (°) for the $(Ph_3P)_3 \cdot AgNC_4H_4O_2 \cdot 3CH_2Cl_2$.

Bond lengths (Å)			
Ag(1)–P(1)	2.619(2)	Ag(1)–P(2)	2.561(1)
Ag(1)–P(3)	2.575(2)	Ag(1)–N(1)	2.313(4)
N(1)–C(55)	1.342(7)	N(1)–C(58)	1.354(8)
O(1)–C(55)	1.216(7)	O(2)–C(58)	1.205(7)
C(55)–C(56)	1.524(8)	C(57)–C(56)	1.490(9)
C(57)–C(58)	1.511(9)	P(1)–C(1)	1.830(5)
P(1)–C(7)	1.824(6)	P(1)–C(13)	1.831(5)
P(2)–C(19)	1.818(6)	P(2)–C(31)	1.821(6)
P(2)–C(25)	1.830(5)	P(3)–C(37)	1.820(5)
P(3)–C(49)	1.823(5)	P(3)–C(43)	1.824(6)
Bond angles (°)			
N(1)–Ag(1)–P(2)	116.5(1)	C(32)–C(31)–P(2)	119.7(5)
N(1)–Ag(1)–P(3)	94.9(1)	C(36)–C(31)–P(2)	121.7(5)
P(2)–Ag(1)–P(3)	113.3(5)	C(38)–C(37)–P(3)	118.0(4)
N(1)–Ag(1)–P(1)	107.3(1)	C(42)–C(37)–P(3)	123.0(4)
P(2)–Ag(1)–P(1)	113.7(5)	C(44)–C(43)–P(3)	124.1(5)
P(3)–Ag(1)–P(1)	109.5(5)	C(48)–C(43)–P(3)	116.6(5)
C(7)–P(1)–C(1)	102.8(2)	O(1)–C(55)–N(1)	126.1(6)
C(7)–P(1)–C(13)	101.9(2)	O(1)–C(55)–C(56)	122.6(6)
C(7)–P(1)–Ag(1)	113.9(2)	N(1)–C(55)–C(56)	111.2(6)
C(1)–P(1)–Ag(1)	116.9(2)	C(57)–C(56)–C(55)	103.8(5)
C(13)–P(1)–Ag(1)	117.7(2)	C(8)–C(7)–P(1)	118.2(4)
C(19)–P(2)–C(31)	103.3(3)	C(20)–C(19)–P(2)	119.0(4)
C(19)–P(2)–C(25)	102.8(2)	C(24)–C(19)–P(2)	123.3(5)
C(19)–P(2)–Ag(1)	115.2(2)	C(55)–N(1)–Ag(1)	123.5(4)
C(31)–P(2)–Ag(1)	121.1(2)	C(58)–N(1)–Ag(1)	124.1(4)
C(25)–P(2)–Ag(1)	111.1(2)	C(6)–C(1)–P(1)	122.6(4)
C(37)–P(3)–C(49)	102.6(2)	C(2)–C(1)–P(1)	117.7(4)
C(37)–P(3)–C(43)	103.0(3)	C(12)–C(7)–P(1)	124.1(4)
C(37)–P(3)–Ag(1)	114.7(2)	O(2)–C(58)–N(1)	125.6(6)
C(49)–P(3)–Ag(1)	111.7(2)	O(2)–C(58)–C(57)	122.6(7)
C(56)–C(57)–C(58)	103.4(6)	N(1)–C(58)–C(57)	111.9(6)
C(55)–N(1)–C(58)	109.6(5)	C(43)–P(3)–Ag(1)	120.6(2)

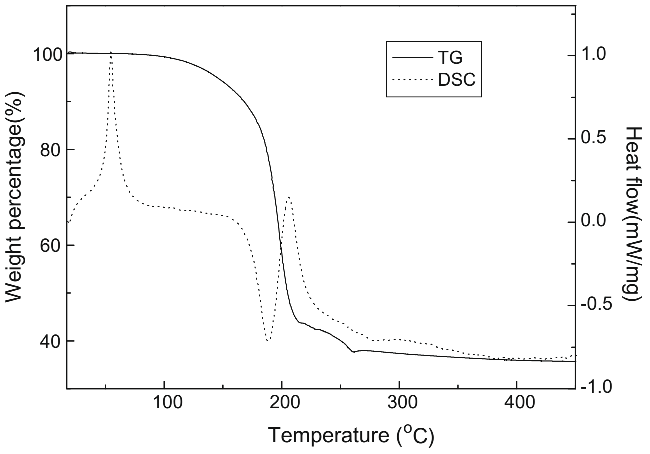


Fig. 2. TG and DSC curves of **2d** (heating rate 10 °C min^{-1}, argon atmosphere).

2d. There are two continuous exothermic/endothermic processes from 163 to 210 °C, with peak temperatures of 189 and 207 °C. As seen from the TG curve, it is very difficult to distinguish from one step to another and know the sequence of decomposition of $P(OEt)_3$ and succinimide. The total weight losses are about 65.09%. The final percentage of the residue is 34.91%, which is higher than the theoretical value of silver (29.01%), which may be due to the some impurities in the complex. The complex exhibits a proper thermal decomposition temperature indicating that it could be a promising candidate as a precursor for growing silver films using the chemical vapor deposition technique.

4. Supplementary data

CCDC 687312 contains the supplementary crystallographic data for **2c**. These data can be obtained free of charge via http://www.ccdc.cam.ac.uk/conts/retrieving.html, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or e-mail: deposit@ccdc.cam.ac.uk.

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