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Synthesis and physical and structural characterization of Ag(I)complexes supported by non-fluorinated β -diketonate and related ancillary ligands

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Abstract

A series of Ag(I) complexes, [Ag(X)L], where X is the anion of 2,2,6,6-tetramethyl-3,5-heptanedione (tmhdH), 2,2,7-trimethyl-3,5octanedione (tmodH), 2-sila-2,2,6,6-tetramethyl-3,5- heptanedione (tmshdH), 5-mercapto-2,2,6,6-tetramethyl-4-hepten-3-one (S-tmhdH), 5-mercapto-2,2,7-trimethyl-4-octen-3-one (S-tmodH), or 5-amino-2,2,6,6-tetramethyl-4-hepten-3-one (N-tmhdH) and L = triphenylphosphine (PPh₃) or tri-*n*-butylphosphine (PBu₃), were prepared by treatment of silver nitrate with either the diketone derivative in the presence of a base or with the preformed sodium salt of the diketone derivative. The thermal properties of the new complexes were investigated for potential application in chemical vapor deposition (CVD) processes. Results of thermogravimetric analysis showed that the vast majority of the silver complexes have little promise for CVD, since the ligands dissociate at elevated temperatures without volatilization. The first ever reported single crystal X-ray diffraction studies of silver complexes, with simple, ancillary, non-fluorinated β -diketonate supporting ligands, revealed [Ag(tmhd)(PPh₃)] (1a) to be monomeric and [Ag(S-tmhd)(PPh₃)]₂ (4a) to be dimeric in the solid state, respectively. © 2002 Elsevier Science Ltd. All rights reserved.

Keywords: Silver(I) complexes; Non-fluorinated β -diketonate ligands; Monothio- β -ketonate; β -Ketoiminate; Chemical vapor deposition; Crystal structures

1. Introduction

Currently, there is ongoing interest in the search for electroluminescent materials. Applications range from lighting appliances, such as fluorescent tubes, to display apparatus such as cathode ray tubes or projection television [1]. One of the most rapidly advancing and growing areas is the development of thin film electroluminescent displays. Inorganic phosphor materials currently are widely used in these applications, while research on organic phosphors is ongoing [2]. The most commonly employed phosphor, the ZnS–Mn with SrS– Ce combination, generates red and green output by filtering the yellow emission from the ZnS–Mn couple while the SrS–Ce couple provides a bluish green light [3]. Unfortunately, the SrS–Ce couple is only a weak blue emitter and as such, a need remains for the development of brighter blue sources. Recent work suggests SrS–Cu is a suitable alternative, with a good blue emission with CIE color coordinates of x = 0.15 and y = 0.23 [3,4]. Codoping of the SrS–Cu couple with Ag gave an even truer blue color with $\text{CIE}_x = 0.17$, $\text{CIE}_y = 0.13$ [3,5]. However, the strategy for silver doping is currently limited by a lack of suitable volatile silver-containing precursors.

One of the techniques for preparation of thin films of these phosphors is metallo-organic chemical vapor deposition (MOCVD). As such, precursor volatility and stability are important issues for doping strategy. Research on the preparation of stable, yet volatile, complexes is central to the development of new, more efficient MOCVD precursors.

 β -Diketonates and allied derivatives are among the most common ancillary ligand types for the preparation

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of MOCVD precursors. Structural variations of the supporting β -diketonate ligand can impart desired chemical and physical properties to the precursor complex as well as modulate the volatility. Introduction of a second, supporting ligand in a ternary complex can have complementary effects, while improving the stability of the complex. Combination of both strategies clearly can lead to highly desirable enhancements in performance for MOCVD.

Previously, the preparation of silver β -diketonate complexes for use in MOCVD have focused on fluorinated β-diketonate ligands, such as hfac (anion of 1,1,1,5,5,5-hexafluoro-2,4-pentanedione) and fod (anion of 2,2-dimethyl-6,6,7,7,8,8,8-heptafluoro-3,5-octanedione) [6]. While these ligands impart volatility to the Ag complexes, a crucial property for applications in MOCVD, fluoride ion contamination in the resultant films is frequently observed. The initial aim of the present study was to investigate alternatives to the use of fluorinated silver β-diketonates for MOCVD applications. Although there were some previous studies that indicated that silver complexes containing non-fluorinated β -diketonate ligands had limited volatility [7], we decided to explore a much wider range of structural alterations to the β -diketonate backbone, including unsymmetrically substituted ligands, as well as those in which silvlated substituents were incorporated or in which an oxygen donor atom was replaced by sulfur [8] or imino nitrogen [9]. The replacement of one of the oxygen donor atoms of the β -diketonate was investigated, since such ancillary ligands might facilitate reduction of oxygen contamination, which accompanies the MOCVD processing of silver β -diketonates. We report here the synthesis and physical characterization of a series of binary and ternary silver complexes, [Ag(X)] and [Ag(X)L], where X is the anion of 2,2,6,6tetramethyl-3,5-heptanedione (tmhdH), 2,2,7-trimethyl-3,5-octanedione (tmodH), 2,2,6,6-tetramethyl-2-sila-3,5-(tmshdH), 5-mercapto-2,2,6,6-tetraheptanedione methyl-4-hepten-3-one (S-tmhdH), 5-mercapto-2,2,7trimethyl-4-octen-3-one (S-tmodH), or 5-amino-2,2,6,6-tetramethyl-4-hepten-3-one (N-tmhdH) and L is triphenylphosphine (PPh₃) or tri-n-butylphosphine (PBu₃). We also present structural results on the first two non-fluorinated β-diketonate silver complexes characterized by single crystal X-ray diffraction.

2. Experimental

2.1. Materials and physical measurements

Unless otherwise noted, all experiments were performed under an inert atmosphere of nitrogen utilizing standard Schlenk techniques or in a Vacuum Atmospheres drybox filled with nitrogen. Reagents and solvents obtained commercially were of reagent grade and used as received unless otherwise noted. Tetrahydrofuran (thf), toluene, and anhydrous diethyl ether (Et₂O) were distilled from sodium-benzophenone ketyl under nitrogen. Pentane and hexane were distilled from sodium-benzophenone-diglyme under nitrogen. The β diketone tmshdH was prepared according to our procedure [10], while tmodH was made analogously by condensing 3-methylbutyryl chloride with pinacolone in the presence of lithium diisopropylamide. The heteroatom substituted β -diketone derivatives, *S*-tmhd [8], *S*tmod [8], and *N*-tmhd [9] were prepared by literature procedures. The sodium salts of the β -diketonate compounds were prepared by modification of the literature procedure for Na(hfac) [11].

¹H, ¹³C, and ¹⁹F NMR spectra were recorded on a Gemini-300 MHz NMR spectrometer at 300, 75.46, and 282.3 MHz, respectively. TGA data were obtained on a TA Instrument TGA 2050 Thermogravimetric Analyzer. Sample sizes were 1–3 mg. The ramp rate was 5.0° min⁻¹ and the nitrogen purge rate was 100 cm³ min⁻¹. Elemental analyses were performed by MHW Laboratories.

2.2. [Ag(tmhd)] (1)

This complex was prepared following a slight modification of the literature procedure [12]. Under an inert atmosphere, a stirring slurry of AgNO₃ (0.42 g, 2.5 mmol) in acetonitrile (0.14 ml) and methanol (5 ml) was cooled to 0 °C. To this slurry was added a solution of tmhdH (0.55 ml, 2.6 mmol) and triethylamine (0.35 ml, 2.5 mmol) in methanol (5 ml). The mixture was stirred at 0 °C for 1 h and then filtered quickly. The whitecolored silver complex was washed with methanol and dried in vacuo. Yield: 0.40 g (55%). *Anal.* Calc. for $C_{11}H_{19}AgO_2$: C, 45.38; H, 6.58. Found: C, 45.52; H, 6.39%. ¹H NMR (C₆D₆): δ 5.71 (s, 1H, C(O)CHC(O)), 1.06 (s, 18H, ^{*t*}Bu-CH₃). ¹³C NMR (C₆D₆): δ 201.6 (*C*= O), 90.7 (C(O)CHC(O)), 39.4 (*C*(CH₃)₃), 27.4 (C(CH₃)₃).

2.3. $[Ag(tmhd)(PPh_3)]$ (1a) (method A)

A stirred slurry of **1** (0.21 g, 0.72 mmol) and triphenylphosphine (0.19 g, 0.71 mmol) in toluene (10 ml) was cooled to 0 °C. The mixture was stirred at 0 °C for 1 h giving a clear solution. Removal of the solvent in vacuo afforded the silver complex as an off-white solid. Yield: 0.33 g (83%). *Anal.* Calc. for C₂₉H₃₄AgO₂P: C, 62.94; H, 6.19. Found: C, 62.78; H, 6.09%. ¹H NMR (C₆D₆): δ 7.28–6.88 (m, 15H, C₆H₅), 6.06 (s, 1H, C(O)CHC(O)), 1.49 (s, 18H, ^tBu–CH₃). ¹³C NMR (C₆D₆): δ 200.4 (C=O), 134.3 (d, ²J_{CP} = 17.0 Hz, *o*-C Ph), 132.1 (d, ¹J_{CP} = 35.8 Hz, *ipso-C* Ph), 130.4 (*p*-C

Ph), 129.0 (${}^{3}J_{CP} = 10.4$ Hz, *m*-*C* Ph), 88.5 (C(O)*C*HC-(O)), 42.4 (*C*(CH₃)₃), 29.4 (C(*C*H₃)₃).

2.4. $[Ag(tmhd)(PPh_3)]$ (1a) (method B)

Na(tmhd) (0.45 g, 2.2 mmol) was dissolved in Et₂O (15 ml) and added to a stirred slurry of AgNO₃ (0.37 g, 2.2 mmol) and triphenylphosphine (0.57 g, 2.2 mmol) in Et₂O (15 ml). The mixture was allowed to react for 24 h forming a gray slurry. The volatile components were removed in vacuo affording the crude product. Extraction with toluene (2 × 20 ml), followed by filtration and evaporation in vacuo, gave the silver complex as a white solid. Yield: 1.2 g (56%). The ¹H NMR spectrum of the product was identical to that formed via Method A.

2.5. $[Ag(tmhd)(PBu_3)]$ (1b)

Tri-*n*-butylphosphine (1.0 ml, 4.0 mmol) was added to a stirred slurry of 1 (1.2 g, 4.0 mmol) in toluene (45 ml) at 0 °C. The mixture was stirred at 0 °C for 1 h giving a red–brown solution. Removal of the toluene in vacuo afforded the silver complex as a reddish brown oily liquid. Yield: 1.8 g (93%). *Anal.* Calc. for C₂₃H₄₆AgO₂P: C, 55.98; H, 9.40. Found: C, 55.82; H, 9.29%. ¹H NMR (C₆D₆): δ 5.82 (s, 1H, C(O)CHC(O)), 1.42 (s, 18H, ^{*t*}Bu–CH₃), 1.32–1.22 (m, 18H, PCH₂CH₂-CH₂CH₃), 0.88 (t, 9H, ³J_{HH} = 6.9 Hz, PCH₂CH₂CH₂-CH₃). ¹³C NMR (C₆D₆): δ 198.9 (C=O), 87.2 (C(O)CHC(O)), 42.1 (C(CH₃)₃), 29.5 (C(CH₃)₃), 27.9 (d, ³J_{CP} = 6.0 Hz, PCH₂CH₂CH₂CH₃), 25.9 (d, ¹J_{CP} = 14.8 Hz, PCH₂CH₂CH₂CH₂CH₃), 24.7 (d, ²J_{CP} = 13.8 Hz, PCH₂CH₂CH₂CH₂CH₃), 14.0 (PCH₂CH₂CH₂CH₃).

2.6. [Ag(tmod)] (2)

This complex was prepared using a similar procedure as that for 1, starting with AgNO₃ (0.51 g, 3.0 mmol) and tmodH (0.59 g, 3.2 mmol). Yield of white solid: 0.57 g (66%). *Anal.* Calc. for C₁₁H₁₉AgO₂: C, 45.38; H, 6.58. Found: C, 45.58; H, 6.54%. ¹H NMR (C₆D₆): δ 5.43 (s, 1H, C(O)CHC(O)), 2.12–1.96 (m, 1H, ^{*i*}Bu–CH), 1.93 (s, 1H, ^{*i*}Bu–CH₂), 1.91 (br s, 1H, ^{*i*}Bu–CH₂), 1.05 (s, 9H, ^{*i*}Bu–CH₃), 0.80 (d, 6H, ³J_{HH} = 6.6 Hz, ^{*i*}Bu–CH₃). ¹³C (C₆D₆): δ 201.1 (C=O), 194.1 (C=O), 95.9 (C(O)CHC(O)), 47.7 (^{*i*}Bu–CH₂), 39.3 (C(CH₃)₃), 27.3 (C(CH₃)₃), 26.2 (^{*i*}Bu–CH), 22.5 (^{*i*}Bu–CH₃).

2.7. $[Ag(tmod)(PPh_3)]$ (2a)

This complex was prepared by a similar method to that for the preparation of **1a** (Method A). Triphenylphosphine (0.12 g, 0.46 mmol) was added to a stirred slurry of **2** (0.13 g, 0.46 mmol) in toluene (15 ml) at 0 °C. The mixture was stirred at 0 °C for 1 h, after which the toluene was removed in vacuo. Trituration of

the oily residue with pentane gave the silver complex as a gray solid. Yield: 0.20 g (79%). Anal. Calc. for $C_{29}H_{34}AgO_2P$: C, 62.94; H, 6.19. Found: C, 62.77; H, 6.24%. ¹H NMR (C₆D₆): δ 7.28–6.86 (m, 15H, C₆H₅), 5.82 (s, 1H, C(O)CHC(O)), 2.60–2.45 (m, 1H, ^{*i*}Bu– CH), 2.41 (br s, 2H, ^{*i*}Bu–CH₂), 1.47 (s, 9H, ^{*t*}Bu– CH₃), 1.12 (d, 6H, ³J_{HH} = 6.0 Hz, ^{*i*}Bu–CH₃). ¹³C NMR (C₆D₆): δ 199.9 (C=O), 194.1 (C=O), 134.3 (d, ²J_{CP} = 16.9 Hz, o-C Ph), 131.9 (d, ¹J_{CP} = 36.8 Hz, *ipso*-C Ph), 130.5 (d, ⁴J_{CP} = 1.9 Hz, p-C Ph), 129.0 (d, ³J_{CP} = 10.7 Hz, m-C Ph), 94.3 (C(O)CHC(O)), 53.2 (^{*i*}Bu–CH₂), 41.9 (C(CH₃)₃), 29.3 (C(CH₃)₃), 27.2 (^{*i*}Bu– CH), 23.3 (^{*i*}Bu–CH₃).

2.8. $[Ag(tmod)(PBu_3)]$ (2b)

This complex was prepared by a similar method to that for **1b**, instead utilizing tri-*n*-butylphosphine (0.11 ml, 0.42 mmol) and **2** (0.13 g, 0.46 mmol). Yield of reddish-black oily liquid: 0.20 g (97%). *Anal.* Calc. for $C_{23}H_{46}AgO_2P$: C, 55.98; H, 9.40. Found: C, 56.12; H, 9.30%. ¹H NMR (C_6D_6): δ 5.66 (s, 1H, C(O)CHC(O)), 2.51–2.36 (m, 1H, ^{*i*}Bu–CH,), 2.29 (br s, 2H, ^{*i*}Bu–CH₂), 1.38 (s, 9H, ^{*i*}Bu–CH₃), 1.21–1.01 (complex, 24H, PCH₂CH₂CH₂CH₃ and ^{*i*}Bu–CH₃), 0.80 (t, 9H, ³J_{HH} = 6.9 Hz, PCH₂CH₂CH₂CH₂CH₃). ¹³C NMR (C₆D₆): 199.3 (*C*=O), 193.5 (*C*=O), 93.9 (C(O)CHC(O)), 53.1 (^{*i*}Bu–CH₂), 41.6 (*C*(CH₃)₃), 29.2 (C(CH₃)₃), 27.9 (d, ³J_{CP} = 5.6 Hz, PCH₂CH₂CH₂CH₂CH₃), 27.1 (^{*i*}Bu–CH), 25.7 (d, ¹J_{CP} = 18.4 Hz, PCH₂CH₂CH₂CH₃), 24.4 (d, ²J_{CP} = 14.2 Hz, PCH₂CH₂CH₂CH₃), 23.3 (^{*i*}Bu–CH₃), 13.8 (PCH₂CH₂CH₂CH₃).

2.9. [Ag(tmshd)] (3)

A mixture of AgNO₃ (0.92 g, 5.4 mmol) in CH₃CN (0.5 ml) and CH₃OH (11 ml) at 0 °C was transferred by cannula to a cooled flask containing a stirring mixture of tmshdH (1.15 g, 5.7 mmol), triethylamine (0.8 ml, 5.7 mmol), and CH₃OH (11 ml) at 0 °C. Immediate formation of white precipitate was observed. The mixture was stirred at 0 °C for an hour, filtered and the precipitates washed with minute amounts of cold CH₃OH. The pale colored precipitates darkened over time even at -25 °C and were used immediately for the preparation of the ternary complex **3a**. Yield: 0.33 g (20%).

2.10. $[Ag(tmshd)(PPh_3)]$ (3a)

A mixture of **3** (0.14 g, 0.46 mmol) and triphenylphosphine (0.12 g, 0.46 mmol) in Et₂O (30 ml) was stirred at 0 °C for 3 h. Removal of the solvent at 0 °C gave a light brown powder. Yield: 0.25 g (95%). *Anal.* Calc. for C₂₈H₃₄AgO₂PSi: C, 59.05; H, 6.02. Found: C, 59.27; H, 5.99%. ¹H NMR (CDCl₃): δ 7.50–7.34 (m, 15H, C₆H₅), 5.80 (s, 1H, C(O)CHC(O)), 1.16 (s, 9H, ^{*t*}Bu–CH₃), 0.17 (s, 9H, Si–CH₃).

2.11. [Ag(S-tmhd)] (4)

A yellow slurry of AgNO₃ (0.26 g, 1.5 mmol) and Na(S-tmhd) (0.34 g, 1.5 mmol) in thf (20 ml) was stirred for 24 h giving a dark gray mixture. The solvent was removed in vacuo and the residue extracted with toluene (20 ml). Filtration and removal of all volatiles in vacuo gave the silver complex as a yellow brown solid. Yield: 0.38 g (81%). *Anal.* Calc. for C₁₁H₁₉AgOS: C, 43.01; H, 6.23. Found: C, 42.91; H, 6.02%. ¹H NMR (CDCl₃): δ 6.74 (s, 1H, C(O)CHC(S)), 1.31 (s, 9H, ^{*t*}Bu–CH₃), 1.10 (s, 9H, ^{*t*}Bu–CH₃). ¹³C NMR (CDCl₃): δ 206.9 (*C*=O), 173.5 (*C*=S), 118.2 (C(O)CHC(S)), 44.7 (*C*(CH₃)₃), 42. (*C*(CH₃)₃), 31.0 (C(*C*H₃)₃), 27.2 (C(*C*H₃)₃).

2.12. $[Ag(S-tmhd)(PPh_3)]$ (4a)

A slurry of AgNO₃ (0.26 g, 1.5 mmol), Na(S-tmhd) (0.33 g, 1.5 mmol) and triphenylphosphine (0.39 g, 1.5 mmol) in thf (20 ml) was stirred for 44 h giving a lemon vellow slurry. The solvent was removed in vacuo and the residue extracted with toluene (25 ml). Filtration and removal of all volatiles in vacuo gave the silver complex as a lemon yellow solid. Yield: 0.61 g (72%). Anal. Calc. for C₂₉H₃₄AgOPS: C, 61.16; H, 6.02. Found: C, 61.32; H, 6.15%. ¹H NMR (CDCl₃): δ 7.60–7.30 (m, 15H, C₆H₅), 6.85 (s, 1H, C(O)CHC(S)), 1.36 (s, 9H, ^tBu-CH₃), 1.14 (s, 9H, ^{*t*}Bu–CH₃). ¹³C NMR (CDCl₃): δ 205.5 (C=O), 134.1 (d, ${}^{2}J_{CP} = 16.6$ Hz, o-C Ph), 131.4 (d, ${}^{1}J_{CP} = 34.6$ Hz, *ipso-C* Ph), 130.6 (d, ${}^{4}J_{CP} = 1.9$ Hz, *p*-*C* Ph), 128.9 (d, ${}^{3}J_{CP} = 10.4$ Hz, *m*-*C* Ph), 113.6 (C(O)CHC(S)), 44.5 (C(CH₃)₃), 44.4 (C(CH₃)₃), 31.5 (C(CH₃)₃), 27.7 (C(CH₃)₃).

2.13. $[Ag(S-tmhd)(PBu_3)]$ (4b)

A mixture of AgNO₃ (0.20 g, 1.2 mmol), Na(*S*-tmhd) (0.26 g, 1.2 mmol) and tri-*n*-butylphosphine (0.30 g, 1.1 mmol) in thf (20 ml) was stirred for 24 h giving a yellow mixture. The solvent was removed in vacuo and the residue extracted with toluene (20 ml). Filtration and removal of all volatiles in vacuo gave the silver complex as a yellow brown oil. Yield: 0.56 g (96%). *Anal.* Calc. for C₂₃H₄₆AgOPS: C, 54.22; H, 9.10. Found: C, 54.42; H, 8.86%. ¹H NMR (CDCl₃): δ 6.74 (s, 1H, C(O)C*H*C(S)), 1.61–1.32 (complex, 18H, PC*H*₂C*H*₂-C*H*₂CH₃), 1.29 (s, 9H, ^{*t*}Bu–C*H*₃), 1.07 (s, 9H, ^{*t*}Bu– C*H*₃), 0.85 (t, 9H, ³*J*_{HH} = 7.2 Hz, PCH₂CH₂CH₂C*H*₂C*H*₃). ¹³C NMR (CDCl₃): δ 204.8 (*C*=O), 185.0 (*C*=S), 113.4 (C(O)CHC(S)), 43.7 (*C*(CH₃)₃), 43.5 (*C*(CH₃)₃), 30.8 (C(CH₃)₃), 27.2 (d, ³*J*_{CP} = 5.6 Hz, PCH₂CH₂CH₂CH₂CH₃), 27.1 (C(CH₃)₃), 24.8 (d, ¹*J*_{CP} = 18.8 Hz, PCH₂CH₂- CH₂CH₃), 23.7 (d, ${}^{2}J_{CP} = 14.3$ Hz, PCH₂CH₂CH₂CH₂CH₃), 13.1 (PCH₂CH₂CH₂CH₃).

2.14. [Ag(S-tmod)] (5)

This complex was prepared by the same method as for **4**, instead using AgNO₃ (0.26 g, 1.5 mmol) and Na(*S*-tmod) (0.34 g, 1.53 mmol). Yield of dark yellow brown product: 0.36 g (76%). *Anal.* Calc. for C₁₁H₁₉AgOS: C, 43.01; H, 6.23. Found: C, 43.18; H, 6.03%. ¹H NMR (CDCl₃): δ 6.48 (s, 1H, C(O)CHC(S)), 2.34 (s, 1H, ⁱBu-CH₂), 2.32 (s, 1H, ⁱBu-CH₂), 2.24–2.05 (m, 1H, ⁱBu-CH₂), 2.32 (s, 1H, ⁱBu-CH₃), 0.85 (d, 6H, ³J_{HH} = 6.3 Hz, ⁱBu-CH₃). ¹³C NMR (CDCl₃): δ 204.8 (*C*=O), 120.7 (C(O)CHC(S)), 59.3 (ⁱBu-CH₂), 2.2.4 (ⁱBu-CH₃).

2.15. $[Ag(S-tmod)(PPh_3)]$ (5a)

This complex was prepared analogously to **4a** using AgNO₃ (0.26 g, 1.5 mmol), Na(*S*-tmod) (0.33 g, 1.5 mmol) and triphenylphosphine (0.39g, 1.5 mmol). Yield of yellow–brown product: 0.71 g (83%). *Anal.* Calc. for C₂₉H₃₄AgOPS: C, 61.16; H, 6.02. Found: C, 61.34; H, 5.87%. ¹H NMR (CDCl₃): δ 7.46–7.26 (m, 15H, C₆H₅), 6.45 (s, 1H, C(O)CHC(S)), 2.33 (bs, 2H, ⁱBu–CH₂), 2.27–2.04 (m, 1H, ⁱBu–CH), 1.01 (s, 9H, ⁱBu–CH₃), 0.82 (d, 6H, ³J_{HH} = 6.3 Hz, ⁱBu–CH₃). ¹³C NMR (CDCl₃): δ 204.6 (*C*=O), 133.9 (²J_{CP} = 16.6 Hz, *o*-*C* Ph), 131.8 (d, ¹J_{CP} = 30.2 Hz, *ipso*-*C* Ph), 130.3 (*p*-*C* Ph), 128.8 (d, ³J_{CP} = 10.0 Hz, *m*-*C* Ph), 117.6 (C(O)CHC(S)), 59.7 (ⁱBu–CH₂), 43.5 (*C*(CH₃)₃), 28.4 (ⁱBu–CH), 27.3 (C(CH₃)₃), 22.3 (ⁱBu–CH₃).

2.16. $[Ag(S-tmod)(PBu_3)]$ (5b)

Na(S-tmod) (0.26 g, 1.2 mmol) was added to a stirring slurry of AgNO₃ (0.20 g, 1.2 mmol) and tri-nbutylphosphine (0.30 ml, 1.1 mmol) in thf (20 ml). The reaction mixture was allowed to react for 24 h, resulting in a gray slurry. The volatile components were removed in vacuo affording the crude product. Extraction with toluene (20 ml) followed by filtration and evaporation in vacuo gave the silver complex as an orange brown oily liquid. Yield: 0.42 g (72%). Anal. Calc. for C₂₃H₄₆AgOPS: C, 54.22; H, 9.10. Found: C, 54.12; H, 9.27%. ¹H NMR (CDCl₃): δ 6.47 (s, 1H, C(O)CHC(S)), 2.33 (s, 1H, ^{*i*}Bu-CH₂), 2.31 (s, 1H, ^{*i*}Bu-CH₂), 2.25-2.05 (m 1H, ^{*i*}Bu-CH), 1.60-1.31 (complex, 18H, PCH₂CH₂- CH_2CH_3), 1.07 (s, 9H, ^tBu- CH_3), 0.80 (d, 6H, ³ $J_{HH} =$ 6.3 Hz, ^{*i*}Bu-CH₂), 0.79 (t, 9H, ³J_{HH} = 7.2 Hz, PCH₂CH₂CH₂CH₃). ¹³C NMR (CDCl₃): δ 203.7 (C= O), 179.2 (C=S), 119.7 (C(O)CHC(S)), 59.8 ($^{i}Bu-CH_{2}$), 43.3 ($C(CH_3)_3$), 28.7 (^{*i*}Bu-CH), 27.6 (d, ³ $J_{CP} = 5.6$ Hz, PCH₂CH₂CH₂CH₃), 27.4 (C(CH₃)₃), 25.5 (d, ${}^{1}J_{CP} =$ 13.6 Hz, $PCH_2CH_2CH_2CH_3$), 24.4 (d, ${}^2J_{CP} = 13.3$ Hz,

PCH₂CH₂CH₂CH₃), 22.5 (t Bu-CH₃), 13.6 (PCH₂CH₂CH₂CH₃).

2.17. $[Ag(N-tmhd)(PPh_3)]$ (6a)

A stirring slurry of AgNO₃ (0.13 g, 0.77 mmol) and Na(N-tmhd) (0.16 g, 0.78 mmol) was dissolved in Et₂O (20 ml). A solution of triphenylphosphine (0.20 g, 0.76 mmol) in Et₂O (40 ml) was added. The reaction mixture was allowed to react for 24 h resulting in a gray slurry. The volatile components were removed in vacuo affording the crude product as a black solid. Extraction with toluene $(2 \times 20 \text{ ml})$ followed by filtration and evaporation in vacuo gave the silver complex as a salmon pink colored solid. Yield: 0.24 g (56%). Anal. Calc. for C₂₉H₃₅AgNOP: C, 63.05; H, 6.39. Found: C, 63.22; H, 6.50%. ¹H NMR (CDCl₃): δ 7.44–7.16 (m, 15H, C₆H₅), 5.32 (s, 1H, C(O)CHC(NH)), 1.14 (s, 9H, ^tBu-CH₃), 1.12 (s, 9H, ^{*t*}Bu–CH₃). ¹³C NMR (CDCl₃): δ 205.3 (C= O), 173.5 (C=NH), 133.8 (d, ${}^{2}J_{CP} = 16.4$ Hz, o-C Ph), 131.8 (d, ${}^{1}J_{CP} = 29.2$ Hz, *ipso-C* Ph), 130.1 (*p-C* Ph), ${}^{3}J_{\rm CP} = 9.8$ Hz, m-CPh), 128.6 (d, 86.4 (C(O)CHC(NH)), 41.9 (C(CH₃)₃), 35.9 (C(CH₃)₃), 28.7 (C(CH₃)₃), 27.8 (C(CH₃)₃).

2.18. $[Ag(N-tmhd)(PBu_3)]$ (6b)

A stirred mixture of AgNO₃ (0.20 g, 1.18 mmol) and (N-tmhd) (0.24 g, 1.18 mmol) was dissolved in thf (10 ml). Tri-*n*-butylphosphine (0.31 ml, 1.18 mmol) was added and the mixture stirred for 18 h. All volatiles were removed from the resulting greenish black mixture. Extraction of the residue with toluene $(2 \times 20 \text{ ml})$ followed by filtration and evaporation in vacuo gave the silver complex as a reddish brown oil. Yield: 0.51 g (88%). Anal. Calc. for C₂₃H₄₇AgNOP: C, 56.10; H, 9.62. Found: C, 55.95; H, 9.49%. ¹H NMR (CDCl₃): δ 10.2 (br s, 1H, NH), 5.18 (s, 1H, C(O)CHC(NH)), 1.53–1.21 (complex, 18H, PCH₂CH₂CH₂CH₃), 1.04 (s, 9H, ^tBu- CH_3), 0.98 (s, 9H, ^tBu-CH₃), 0.75 (t, 9H, ³J_{HH} = 6.9 Hz, PCH₂CH₂CH₂CH₃). ¹³C NMR (CDCl₃): δ 204.9 (C=O), 173.4 (C=NH), 86.2 (C(O)CHC(NH)), 41.7 $(C(CH_3)_3)$, 35.8 $(C(CH_3)_3)$, 28.6 $(C(CH_3)_3)$, 27.7 $(C(CH_3)_3)$, 27.4 (d, ${}^{3}J_{CP} = 2.9$ Hz, $PCH_2CH_2CH_2CH_3)$, 24.8 (d, ${}^{1}J_{CP} = 16.6$ Hz, $PCH_2CH_2CH_2CH_3$), 24.0 (d, $^{2}J_{\rm CP} = 13.5$ $PCH_2CH_2CH_2CH_3),$ Hz, 13.3 $(PCH_2CH_2CH_2CH_3).$

2.19. X-ray crystallography

Crystals of **1a** and **4a** suitable for X-ray diffraction studies were obtained by dissolving the corresponding complex in thf and layering pentane over the solution. The mixture was cooled to -35 °C, while allowing the pentane to diffuse slowly through the mixture. Crystals formed over a period of five to nine days (yield of **1a**:

30%; yield of **4a**: 75%). X-ray data were collected at ambient temperature using a Bruker R3m diffractometer in the $\omega - 2\theta$ mode with variable scan speed $(3-20 \circ \text{min}^{-1})$ and graphite monochromated Mo K α radiation ($\lambda = 0.71073$ Å). Check reflections were measured every 200 reflections during data collection and gave no indication of crystal decay. Data were corrected for background, attenuators, Lorentz and polarization effects in the usual fashion [13]. A semi-empirical absorption correction was applied to **4a** using the Ψ scan method.

Both structures were solved by direct methods and refined by full matrix least-squares procedures on $|F^2|$ with the SHELXTL Plus package of programs. All nonhydrogen atoms were refined anisotropically; hydrogen atom positions were calculated geometrically and fixed at a C-H distance of 0.96 Å and were not refined. Crystal data and further data collection parameters are summarized in Table 1.

Table 1 Crystallographic data and parameters for **1a** and **4a**

	1a	4a
Formula	C ₂₉ H ₃₄ AgO ₂ P	$C_{58}H_{68}Ag_2O_2P_2S_2$
Formula weight	553.4	1138.9
Crystal color, Habit	Pale yellow, plate	Pale yellow, rectangular
	•	prism
Crystal dimensions	0.15 imes 0.30 imes 0.45	$0.15 \times 0.20 \times 0.45$
(mm)		
Crystal system	monoclinic	triclinic
Space group	$P2_1/c$	ΡĪ
a (Å)	13.253(6)	11.194(3)
b (Å)	11.756(3)	13.639(3)
c, (Å)	17.722(5)	20.431(5)
α (°)	90	75.32(2)
β(°)	102.40(3)	78.61(2)
γ (°)	90	72.37(2)
$V Å^3$	2696.7(16)	2851.0(12)
Ζ	4	2
$D_{\rm calc} ({\rm g}{\rm cm}^{-3})$	1.363	1.327
μ (Mo K α) (cm ⁻¹)	8.29	8.54
F(000)	1144	1176
2θ max (°)	45.0	45.0
Reflections collected	3698	7678
Independent	3521	7427
reflections	$(R_{\rm int} = 1.44\%)$	$(R_{\rm int} = 2.68\%)$
Observed reflections	2081	4351
	$(F > 6.0\sigma(F))$	$(F > 4.0\sigma(F))$
T_{\min}/T_{\max}	N/A	0.868/0.953
Number of	298	595
parameters		
R ^a	0.0422	0.0817
$R_{\rm w}^{\rm a}$	0.0437	0.0826
Goodness-of-fit ^b	1.19	1.51

^a $R = \Sigma ||F_0| - |F_c|| \Sigma |F_0|$; $R_w = [\Sigma w(|F_0| - |F_c|)^2 \Sigma w |F_0|^2]^{1/2}$; $w = 1/\sigma^2(F_0) + g(F_0)^2$; g = 0.001 and 0.002 for **1a** and **4a**, respectively. ^b GOF = $[\Sigma w(|F_0| - |F_c|)^2 / (NO - NV)]^{1/2}$, where NO is the number of observations and NV is the number of variables.

3. Results and discussion

3.1. Synthesis

Two routes were employed for the syntheses of the binary silver complexes, [Ag(X)]. For complexes 1 (X = tmhd), 2 (X = tmod), and 3 (X = tmshd), a modification of the method of Wakeshima [13] was employed. In this approach, AgNO₃ was reacted with the β -diketone in the presence of a base (Eq. (1)). Alternatively for 4 (X = S-tmhd) and 5 (X = S-tmod), the complexes were readily formed by displacement of nitrate using the sodium salt of the β -diketonate derivative (Eq. (2)) [14]. The method described in Eq. (1) was somewhat preferable, in that it afforded spectroscopically pure products, suitable for further reaction with neutral coordinating ligands to form ternary complexes (vide infra). On the other hand, separation of the silver product obtained in Eq. (2) from unreacted sodium β -diketonate was difficult due to the similar solubilities of these substances in most solvents. Attempts to prepare the complexes via reaction of Ag_2O with the β -diketone, as described for hfac [7], failed to provide the desired compounds. This result may be attributed to the decreased acidity of the nonfluorinated β -diketones relative to the fluorinated analogs.



Ternary complexes, [Ag(X)L], were prepared in two ways. In the first method, reaction of Ag(tmhd) 1, Ag(tmod) 2, and Ag(tmshd) 3 with 1 equiv. of PPh₃ or PBu₃ gave the corresponding desired complexes 1a-3a(L = PPh₃) and 1b-2b (L = PBu₃) in > 80% yield. The complexes are air-stable; the PPh₃ derivatives were white to grayish-white in color, while the PBu₃ compounds were orange or reddish-brown viscous liquids, perhaps due to slight amounts of oxidation products. In all cases, good elemental analyses [15] and NMR spectroscopic data were obtained, so contamination must have been quite small. Slight downfield shifts of the CH resonance of the β -diketonate ligands were observed in the ¹H NMR spectra, while slight upfield shifts were found for the carbonyl and CH carbon atoms in the ¹³C NMR spectra, upon coordination of the phosphine ligands. Although slight darkening occurred over long periods of time, no changes were observed in the NMR spectra of the compounds.

Complex **1a** could also be obtained by direct reaction of AgNO₃ with Na(tmhd) in the presence of PPh₃. This method was employed successfully for the preparation of [Ag(X)L], X = S-tmhd, $L = PPh_3$ **4a** or PBu₃ **4b**; X =*S*-tmod, $L = PPh_3$ **5a** or PBu₃ **5b**. The complexes were air-stable, yellow to yellow–brown compounds, probably due to the coloration of the ligands. The ¹H NMR resonance for the CH resonance of the monothio- β diketonate ligands in the silver complexes experienced a downfield shift compared to the corresponding silver β diketonate complexes, a result previously noted by Musso and coworkers for an analogous silver complex [16]. We also observed a downfield shift of the CH resonance in the ¹³C NMR spectra of the coordinated ligands upon sulfur substitution.

Attempts to isolate pure Ag(*N*-tmhd) proved unsuccessful, perhaps due to ease of hydrolysis [17]. However, [Ag(*N*-tmhd)L], $L = PPh_3$ **5a** or PBu₃ **5b** could be prepared in acceptable yield by direct reaction of AgNO₃ with Na(*N*-tmhd) in the presence of the appropriate phosphine ligand. The CH resonance of the β -diketoiminate ligands in **5a** and **5b** was slightly upfield of the chemical shifts observed for the β -diketonate analogs, **1a** and **1b**, in both the ¹H and ¹³C NMR spectra.

3.2. Thermal studies

Thermogravimetric analysis was employed to determine the suitability of the silver complexes for MOCVD processing. Experiments were conducted at atmospheric pressure under a nitrogen purge. Typical temperatures of maximum weight loss were in the range of 160-240 °C. For most of the complexes, weight loss was accompanied by residues in the TGA pan, the amount of which was comparable to the theoretical percentage of silver present in the complex. In fact in some cases, the residue appeared to be a silver mirror. Evidently, these complexes lose the ancillary ligands upon heating, without significant volatilization of the intact complex. One exception was 1b, which had maximum rate of weight loss at 204 °C and a residue of only 11% (theoretical %Ag, 22%). Thus, at atmospheric pressure, the majority of the studied complexes showed little utility for MOCVD applications.

3.3. X-ray diffraction studies

While numerous solid-state structures have been reported for silver complexes supported by fluorinated β -diketonate ligands [6a,6b,6c,6f,6h,6f,6h,7,17–23], we

have determined the first structures of ternary silver complexes containing either a non-fluorinated β -diketonate or a monothio- β -diketonate ligand.

The asymmetric unit for $[Ag(tmhd)(PPh_3)]$ **1a** contains one molecule of the mononuclear complex. The geometry is best described as highly distorted trigonal planar (Fig. 1); selected bond lengths and angles are summarized in Table 2. Ag(1), P(1), O(1), and O(2) are planar to within ± 0.066 Å; the silver atom is 0.18 Å out of the plane defined by the three donor atoms of the ligands.

Structural features for 1a are reminiscent to those reported for similar, three-coordinate analogs, [Ag(hfac)L], $L = PMe_3$ [6a,6b,6c], MeNC [6f], and PPh₃ [17]. Comparisons to the latter complex are probably most fruitful. The silver atom in 1a is unsymmetrically bonded to the tmhd ligand with the Ag(1)-O(1) bond almost 0.08 Å longer than Ag(1)-O(2). Not surprisingly, the longer Ag-O bond occurs on the side of the complex with the smaller P-Ag-O angle (Table 2 and Fig. 1). Similar results are observed for [Ag(hfac)(PPh₃)] [17]. The reasons for these distortions are not clear, though sterics may play a part; the hfac ligand is more symmetrically coordinated in $[Ag(hfac)L], L = PMe_3$ [6a,6b,6c] and MeNC [6f]. The Ag–O bonds in 1a are slightly shorter than those observed for [Ag(hfac)(PPh₃)] (2.218 (5) and 2.341(5) Å) [17], which can be attributed to the absence of the electron-withdrawing trifluoromethyl substituents. However, no appreciable lengthening of the C-O bonds of the tmhd ligand was observed for 1a. The Ag–P bond length in 1a is comparable to those in previously reported monomeric, three-coordinate silver β -diketonate complexes [6a,6b,6c,6f,17]. The packing diagram shows a head-to-tail stacking of βdiketone ligands for adjacent molecules. Stacking of phenyl rings is also observed for alternating molecules.

The asymmetric unit for $[Ag(S-tmhd)(PPh_3)]$ 4a contains two crystallographically independent halves

Fig. 1. Molecular structure and atom numbering scheme for 1a.

Table 2 Selected bond lengths (Å) and angles (°) for **1a**

Bond lengths		
Ag(1) - P(1)	2.320(2)	
Ag(1) - O(1)	2.176(5)	
Ag(1) - O(2)	2.254(6)	
O(1) - C(1)	1.260(8)	
O(2)-C(3)	1.257(8)	
C(1)-C(2)	1.385(11)	
C(2)-C(3)	1.417(10)	
Bond angles		
P(1)-Ag(1)-O(1)	152.3(2)	
P(1)-Ag(1)-O(2)	122.7(2)	
O(1) - Ag(1) - O(2)	82.5(2)	
Ag(1) - O(1) - C(1)	130.0(5)	
Ag(1) - O(2) - C(3)	128.8(5)	
C(1)-C(2)-C(3)	127.7(6)	

of centrosymmetric dimers; thus, the triclinic unit cell contains two dimers. Selected bond lengths and angles are collected in Table 3. To our knowledge, **4a** is the first complex for which a monothio- β -diketonate serves as a bridging ligand [24,25], though a weak, long-range bridging interaction is observed in a Hg(II) monothio- β -diketonate complex [9].

The two dimers of **4a** have similar overall structures (see Fig. 2 for dimer molecule 1). The *S*-tmhd ligands in both **4a** dimers can be considered to be bridging in a $\mu_4:\eta^2,\eta^2$ mode, that is analogous to that seen for the hfac ligands in [Ag(hfac)L]₂, where L is 1,5-dimethyl-1,5-cyclooctadiene [18] or diglyme [19a]. The dihedral angle between the planes defined by the bridging *S*tmhd ligands in each dimer is a crystallographicallyenforced 0.00°. The Ag···Ag distances in the dimers are

Table 3 Selected bond lengths (Å) and angles (°) for 4a

Molecule 1			
Ag(1) - P(1)	2.382(3)	P(1)-Ag(1)-S(1)	132.6(1)
Ag(1) - S(1)	2.540(4)	P(1)-Ag(1)-O(1)	118.2(2)
Ag(1) - O(1)	2.604(9)	S(1) - Ag(1) - O(1)	75.9(2)
Ag(1)-S(1a)	2.608(4)	P(1)-Ag(1)-S(1a)	116.7(1)
Ag(1)-O(1a)	2.830(9)	P(1)-Ag(1)-O(1a)	126.0(2)
S(1)-C(1)	1.720(13)	S(1) - Ag(1) - S(1a)	110.7(1)
O(1) - C(3)	1.335(16)	O(1)-Ag(1)-O(1a)	114.9(2)
C(1) - C(2)	1.364(21)	Ag(1)-S(1)-C(1)	115.2(4)
C(2)-C(3)	1.435(18)	Ag(1) - O(1) - C(3)	119.6(7)
Molecule 2			
Ag(1')-P(1')	2.372(3)	P(1')-Ag(1')-S(1')	130.7(1)
Ag(1')-S(1')	2.540(4)	P(1')-Ag(1')-O(1')	117.0(2)
Ag(1') - O(1')	2.575(9)	S(1')-Ag(1')-O(1')	77.4(2)
Ag(1')-S(1'a)	2.634(5)	P(1')-Ag(1')-S(1'a)	117.4(1)
Ag(1')-O(1'a)	2.750(9)	P(1')-Ag(1')-O(1'a)	128.2(2)
S(1')-C(1')	1.624(16)	S(1')-Ag(1')-S(1'a)	111.8(1)
O(1')-C(3')	1.499(18)	O(1')-Ag(1')-O(1'a)	114.1(2)
C(1')-C(2')	1.376(19)	Ag(1')-S(1')-C(1')	117.5(4)
C(2') - C(3')	1.446(17)	Ag(1')-O(1')-C(3')	115.7(7)



Fig. 2. Molecular structure for and atom numbering scheme for dimer molecule 1 for **4a**. Hydrogen atoms are omitted for clarity.

2.929(2) and 2.900(2) Å, for dimer molecules 1 and 2, respectively.

The Ag–S bond lengths for the dimers of 4a are clearly within bonding range, but are somewhat longer on average than those observed in silver clusters containing bridging thiolate ligands [26] or for metalto-sulfur bond distances in comparable, monomeric monothio-\beta-diketonate complexes involving metals from the second and third transition series [9,24]. The Ag–O distances are longer than the Ag–S bonds and include one long and one very long interaction per silver center from different bridging S-tmhd ligands. These interactions are weak at best; if the longer interaction is ignored, then the geometry about each silver ion is distorted tetrahedral. On the other hand, each silver ion can be considered to be distorted trigonal planar, if all Ag–O bonds are omitted. Interestingly, the shorter Ag– O bond distance is similar to that found in monomeric $[Hg(S-tmhd)_2]$, a linear complex with two weak Hg–O interactions [9]. The Ag-P bond distances in the 4a dimers are somewhat longer than those found for 1a and [Ag(hfac)(PPh₃)] [17], presumably due to increased steric congestion in the dimers.

4. Conclusions

We have presented a series of silver complexes containing non-fluorinated β -diketonate derivatives. These complexes are air-stable, though slightly light and temperature sensitive. We have also reported on the first solid-state structures for this class of complexes, including [Ag(tmhd)(PPh₃)] **1a** and [Ag(S-tmhd)(PPh₃)] **4a**. The former is a monomeric, three-coordinate complex, while the latter is a dimer with two bridging Stmhd ligands.

In general at atmospheric pressure, the complexes under study decompose without volatilization to give silver via loss of the supporting ligands. One exception was 1b, [Ag(tmhd)(PBu₃)], which exhibited some ability to volatilize before total decomposition. We note that while our work was in progress, Edwards, et al. reported on the utility of $[Ag(X)(PPh_3)]$ complexes for CVD processes, where X is various β -diketonate or β -ketoiminate ligands [17]. This group found a significant variation in volatility and quality of deposited silver films as a function of X. While many silver β -diketonate derivatives, [Ag(X)L], including those in the present study, are either too ionic [22] or too unstable to be employed for CVD applications, it appears that judicious choice of X and L ancillary ligands will possibly allow for useful complexes to be obtained [6f,17,20,21].

5. Supplementary material

Full lists of crystallographic data for **1a** (CCDC 169487) and **4a** (CCDC 169488), including atomic coordinates, bond lengths and angles, and anisotropic thermal parameters have been deposited with the Cambridge Crystallographic Data Center. Copies of this information may be obtained from The Director, CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK (fax: +44-1233-336033; e-mail: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk).

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