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Organophosphine/phosphite stabilized disilver(I) methanedisulphonates: synthesis, solid state structures and their potential use as MOCVD precursors[†]

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New disilver(1) methanedisulphonate complexes $[CH_2(SO_3)_2Ag_2 \cdot L_n]$ (L = PPh₃; n = 2, **2a**; n = 3, **2b**; n = 4, **2c**; n = 5, **2d**; n = 6, **2e**; L = P(OEt)₃; n = 2, **2f**; n = 4, **2g**; n = 6, **2h**) were prepared by the reaction of $[CH_2(SO_3)_2Ag_2]$, which could be synthesized from methanedisulphonic acid and Ag₂CO₃ in water, with triphenylphosphine or triethylphosphite in dichloromethane under a nitrogen atmosphere. The solid state structures of three complexes **2c**, **2d** and **2f** were determined by single X-ray structure analysis. Hot-wall metal organic chemical vapor deposition (MOCVD) experiments were carried out at 395 °C, 420 °C and 450 °C using **2g** as precursor for the deposition of silver films, respectively. The silver film with high purity obtained at 420 °C is dense and homogeneous, which is composed of many well isolated, granular particulates spreading all over the substrate surface.

Introduction

Silver exhibits the lowest resistivity and highest thermal conductivity of all metals at room temperature.¹⁻³ Silver plays an important role in many fields of materials science, for example, contacts in microelectronics,⁴ the production of mirrors,⁵ component of hightemperature superconducting materials,⁶ magnetics,⁷ or bactericidal coatings.⁸ Various methods have been used to deposit silver thin films, such as sputtering,⁹ thermal evaporation,¹⁰ electronbeam evaporation,¹¹ and chemical vapor deposition (CVD).¹² Of these techniques, metal organic chemical vapor deposition (MOCVD) is a very effective technique for the contacts in ultra large-scale integration (ULSI) devices and the dopant in hightemperature superconductors, because of its high deposition rates with good step coverage¹³⁻¹⁶ and high aspect ratio in the multilevel metallization structure.¹⁷

The key to achieve success for MOCVD, however, is the selection of suitable precursors. Several inorganic and organometallic precursors, including AgF,¹⁸ [(C₄F₇)Ag]_n,¹⁹⁻²¹ (β -diketonato)Ag(PR₃),²²⁻²⁶ (hfac)Ag(CNMe)²⁷ and various organophosphine stabilized silver carboxylates ²⁸ have been used as MOCVD precursors in a number of studies. Thus, new classes of fluorine-free silver(1) precursors are highly desirable due to less fluorine contamination. Known for good chelating ability, the class of cyclic β -diketones can impart desired chemical and

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physical properties to the precursor complex as well as modulate the volatility. As with cyclic β -diketones, methanedisulphonic acid could lead to precursors with novel six-membered ring system structures however there are only a few reports of these metal complexes.²⁹

Here we describe the synthesis and characterization of a series of organophosphine/phosphite stabilized disilver(1) methanedisulphonates of type $[CH_2(SO_3)_2Ag_2 \cdot L_n]$ (L = PPh₃; n= 2, 2a; n = 3, 2b; n = 4, 2c; n = 5, 2d; n = 6, 2e; L = P(OEt)₃; n = 2, 2f; n = 4, 2g; n = 6, 2h). Complex $\{CH_2(SO_3)_2Ag_2 \cdot [P(OEt)_3]_4\}$ (2g) was tested as a precursor for the deposition of silver by using MOCVD techniques for the first time. The single crystal structures of 2c, 2d and 2f have been determined and discussed as well.

Experimental section

General procedures

All operations were carried out under an atmosphere of purified nitrogen with standard Schlenk techniques. The solvent dichloromethane (CH₂Cl₂) was purified by distillation from P₂O₅ under N₂ before use. ¹H NMR were recorded with a Bruker Advance 300 spectrometer operating at 300.13 MHz in a Fourier transform mode; ¹³C{H} NMR spectra were recorded at 75.47 MHz. Chemical shifts are reported in δ units (parts per million) downfield from tetramethylsilane (δ = 0.0 ppm) with the solvent as the reference signal (¹H NMR, CDCl₃ δ = 7.26; ¹³C{H} NMR, CDCl₃ δ = 77.55). ³¹P{H} NMR spectra were recorded with a Bruker Advance 300 spectrometer operating at 121.49 MHz, using the pulsed Fourier transform mode. ³¹P{H} NMR spectra were run under conditions of broad band proton decoupling in CDCl₃. All spectra were referenced to external 85% H₃PO₄ at

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room temperature, with the appropriate lock solvent. Infrared spectra were collected on a Bruker Vector 22 instrument as KBr pellets at room temperature. Elemental analyses were performed on a Perkin-Elmer 240 C elemental analyzer. Thermogravimetric studies (TG) and differential scanning calorimetric (DSC) studies were carried out with the NETZSCH STA 409 PC/PG with a constant heating rate of 10 °C min⁻¹ under N₂ (30 cm³ min⁻¹). Melting points were observed in sealed capillaries and were uncorrected. The MOCVD experiments were carried out in a vertical quartz tube hot-wall MOCVD reactor, 60 mm in diameter. Heating was achieved by a resistively heated tube oven (AICHUANG Company). The temperature was set by a temperature control FP 93 (SHIMADEN Company) and calibrated with a thermocouple type SR 3 (SHIMADEN Company) digital thermometer. The precursor container was heated with a heating band for evaporation of the precursor. The precursor vapor was transported to the reactor tube by N₂ carrier gas. The carrier gas flow was regulated using a D07-7B (SEVENSTAR Company) mass flow controller which was connected to the apparatus by a section of flexible stainless steel tubing. The pressure control system consisted of a cooling trap and a FT-110 (KYKY Company) molecular pump unit. The trap prevented the reactor effluents from entering the vacuum pump. Scanning electron microscopy (SEM) images and Energy-Dispersion X-ray Spectroscopy (EDX) analysis were carried out by a Hitachi Model S-4800 with scanning electron microscope and energy dispersive X-ray detector.

Synthesis of [CH₂(SO₃)₂Ag₂] (1)

Methanedisulphonic acid (4.58 g, 0.026 mol) dissolved in 30 mL of H_2O was added dropwise into a stirred suspended solution of $[Ag_2CO_3]$ (7.72 g, 0.028 mol) in 20 mL of H_2O at 20 °C. The clear solution was obtained by filtration through a pad of celite after stirring the reaction mixture for 1 h at 20 °C. A white solid product was obtained after removing the water in a rotary evaporator and vacuum drying oven at 50 °C. The product was stored under nitrogen and kept in darkness. Yield: 8.52 g (84%, based on Ag_2CO_3).

Synthesis of [CH₂(SO₃)₂Ag₂·(PPh₃)₂] (2a)

Triphenylphosphine (0.2623 g, 1.00 mmol) dissolved in 20 mL of CH₂Cl₂ was added dropwise into a stirred suspended solution of [CH₂(SO₃)₂Ag₂] (0.1949 g, 0.50 mmol) in 20 mL of CH₂Cl₂ at 0 °C. The 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 *in vacuo* using an oil-pump. Yield: 0.42 g (92%, based on [CH₂(SO₃)₂Ag₂]. M.p. (decomp.): 189 °C. Anal. Calc. for C₃₇H₃₂O₆Ag₂P₂S₂: C, 48.60; H, 3.53. Found: C, 48.53; H, 3.44%. IR (KBr) data (cm⁻¹): 3052 (m), 1479 (m), 1434 (vs), 1243 (s), 1202 (s), 1157 (w), 1095 (m), 1008 (m), 791 (m), 745 (s), 694 (vs), 578 (m), 516 (s). ¹H NMR (CDCl₃): δ 4.2 (s, 2H, CH₂-H), 7.2–7.4 (m, 30H, Ph-H). ¹³C{¹H} NMR (CDCl₃): δ 68.9 (CH₂), 134.0 (J_{PC} = 16.4 Hz, C₆H₅), 131.2 (J_{PC} = 32.7 Hz, C₆H₅), 130.5 (C₆H₅), 129.0 (J_{PC} = 10.0 Hz, C₆H₅). ³¹P{¹H} NMR (CDCl₃): δ 11.5.

Synthesis of [CH₂(SO₃)₂Ag₂·(PPh₃)₃] (2b)

Complex **2b** as a white solid was obtained following the above procedure, only using $[CH_2(SO_3)_2Ag_2]$ (0.1949 g, 0.50 mmol) and

triphenylphosphine (0.3935 g, 1.50 mmol) instead. Yield: 0.55 g (93%, based on [CH₂(SO₃)₂Ag₂]. M.p. (decomp.): 194 °C. Anal. Calc. for C₅₅H₄₇O₆Ag₂P₃S₂: C, 56.14; H, 4.02. Found: C, 56.05; H, 3.94%. IR (KBr) data (cm⁻¹): 3051 (m), 2925 (m), 2853 (m), 1478 (m), 1434 (vs), 1249 (vs), 1202 (vs), 1096 (m), 1064 (w), 1004 (m), 747 (s), 695 (vs), 577 (m), 509 (s). ¹H NMR (CDCl₃): δ 4.1 (s, 2 H, CH₂-H), 7.2–7.4 (m, 45 H, Ph-H). ¹³C{¹H} NMR (CDCl₃): δ 68.9 (CH₂), 134.1 (J_{PC} = 16.2 Hz, C₆H₅), 131.4 (J_{PC} = 31.9 Hz, C₆H₅), 130.6 (C₆H₅), 129.0 (J_{PC} = 9.7 Hz, C₆H₅). ³¹P{¹H} NMR (CDCl₃): δ 11.4.

Synthesis of [CH₂(SO₃)₂Ag₂·(PPh₃)₄] (2c)

Complex **2c** as a white solid was synthesized in the same manner as **2a**. In this respect, $[CH_2(SO_3)_2Ag_2]$ (0.2690 g, 0.69 mmol) was reacted with triphenylphosphine (0.7239 g, 2.76 mmol). Yield: 0.93 g (94%, based on $[CH_2(SO_3)_2Ag_2]$). M.p. (decomp.): 202 °C. Anal. Calc. for $C_{73}H_{62}O_6Ag_2P_4S_2$: C, 60.93; H, 4.34. Found: C, 60.87; H, 4.56%. IR (KBr) data (cm⁻¹): 3052 (m), 1480 (m), 1435 (vs), 1251 (s), 1204 (s), 1096 (m), 1026 (w), 1007 (m), 789 (m), 744 (s), 694 (vs), 578 (m), 505 (s). ¹H NMR (CDCl₃): δ 3.9 (s, 2 H, CH₂), 7.2– 7.4 (m, 60 H, Ph). ¹³C{¹H} NMR (CDCl₃): δ 68.6 (CH₂), 134.1 ($J_{PC} = 16.4$ Hz, C_6H_5), 132.1 ($J_{PC} = 26.5$ Hz, C_6H_5), 130.0 (C_6H_5), 128.8 ($J_{PC} = 9.4$ Hz, C_6H_5). ³¹P{¹H} NMR (CDCl₃): δ 8.0.

Synthesis of [CH₂(SO₃)₂Ag₂·(PPh₃)₅] (2d)

Complex **2d** as a white solid was prepared as described for **2a**, only using $[CH_2(SO_3)_2Ag_2]$ (0.2690 g, 0.69 mmol) and triphenylphosphine (0.9049 g, 3.45 mmol) instead. Yield: 1.08 g (92%, based on $[CH_2(SO_3)_2Ag_2]$). M.p. (decomp.): 208 °C. Anal. Calc. for $C_{91}H_{77}O_6Ag_2P_3S_2$: C, 62.24; H, 4.56. Found: C, 62.15; H, 4.49%. IR (KBr) data (cm⁻¹): 3051 (m), 2926 (m), 1480 (m), 1434 (s), 1242 (s), 1200 (s), 1161 (m), 1095 (m), 1006 (m), 746 (s), 696 (vs), 578 (m), 510 (s). ¹H NMR (CDCl_3): δ 3.9 (s, 2 H, CH₂), 7.2–7.4 (m, 75 H, Ph). ¹³C{¹H} NMR (CDCl_3): δ 68.6 (CH₂), 134.1 (J_{PC} = 16.8 Hz, C₆H₅), 132.8 (J_{PC} = 22.2 Hz, C₆H₅), 129.9 (C₆H₅), 128.8 (J_{PC} = 9.3 Hz, C₆H₅). ³¹P{¹H} NMR (CDCl₃): δ 5.8.

Synthesis of [CH₂(SO₃)₂Ag₂·(PPh₃)₆] (2e)

Complex **2e** as a white solid was prepared following the synthesis of **2a**. In this respect, triphenylphosphine (0.7869 g, 3.00 mmol) was reacted with $[CH_2(SO_3)_2Ag_2]$ (0.1949, 0.50 mmol). Yield: 0.92 g (94%, based on $[CH_2(SO_3)_2Ag_2]$). M.p. (decomp.): 215 °C. Anal. Calc. for $C_{109}H_{92}Ag_2O_6P_6S_2$: C, 66.67; H, 4.72. Found: C, 66.58; H, 4.62%. IR (KBr) data (cm⁻¹): 3051 (m), 1479 (m), 1434 (vs), 1240 (s), 1201 (s), 1093 (m), 1026 (m), 1010 (m), 743 (s), 695 (vs), 579 (m), 514 (s). ¹H NMR (CDCl_3): δ 3.9 (s, 2H, CH₂), 7.2–7.4 (m, 90H, Ph). ¹³C{¹H} NMR (CDCl_3): δ 68.9 (CH₂), 133.9 (J_{PC} = 16.83 Hz, C_6H_5), 133.4 (J_{PC} = 15.52 Hz, C_6H_5), 129.7 (C_6H_5), 128.7 (J_{PC} = 8.73 Hz, C_6H_5). ³¹P{¹H} NMR (CDCl_3): δ 5.0.

Synthesis of $\{CH_2(SO_3)_2Ag_2 \cdot [P(OEt)_3]_2\}$ (2f)

Complex **2f** was synthesized as described earlier (see synthesis of **2a**). In this respect, $[P(OEt)_3]$ (1.8791 g, 11.32 mmol) was reacted with $[CH_2(SO_3)_2Ag_2]$ (2.2067 g, 5.66 mmol). After appropriate work-up, complex **2f** can be isolated as a white solid. Yield: 3.68 g (90%, based on $[CH_2(SO_3)_2Ag_2]$. M.p. (decomp.): 47 °C. Anal.

$Table \ 1 \quad Crystallographic \ data \ for \ complexes \ 2c, \ 2d \ and \ 2f$

	2c	2d	2f
Formula	$C_{73}H_{62}Ag_2O_6P_4S_2 \cdot (C_7H_8, CH_2Cl_2)$	$C_{91}H_{77}Ag_2O_6P_5S_2\cdot 4(CH_2Cl_2)$	$C_{26}H_{64}Ag_4O_{24}P_4S_4$
Formula weight	1616.05	2040.97	1444.37
λ (Mo K α) (Å)	0.71073	0.71073	0.71073
Space group	P-1	$P2_1/n$	P-1
Crystal system	Triclinic	Monoclinic	Triclinic
Z value	2	4	2
a(Å)	12.299(3)	15.329(3)	12.475(3)
$b(\dot{A})$	13.261(3)	21.750(4)	15.116(3)
$c(\dot{A})$	25.321(5)	27.277(6)	16.300(3)
α (°)	99.86(3)	90	64.90(3)
β (°)	97.83(3)	90.39(3)	67.97(3)
γ (°)	111.25(3)	90	74.61(3)
$V(Å^3)$	3702.7(18)	9094(3)	2559.5(12)
D_{calc} (g cm ⁻³)	1.449	1.491	1.874
F(000)	1652	4160	1448
Temperature (K)	153(2)	153(2)	153(2)
Reflections collected	29 033	43 506	17 793
Unique/observed $[I > 2\sigma(I)]$ reflections	13 301/10 663	17 561/15 852	9148/7818
R _{int}	0.048	0.033	0.017
$R_1, WR_2 [I > 2\sigma(I)]$	0.0685, 0.1744	0.0573, 0.1310	0.0221, 0.0531
R_1 , w R_2 (all data)	0.0840, 0.1878	0.0643, 0.1364	0.0267, 0.0545
Goodness-of-fit on F^2	1.067	1.032	1.012

Calc. for C₁₃H₃₂O₁₂Ag₂P₂S₂: C, 21.62; H, 4.47. Found: C, 21.57; H, 4.38%. IR (KBr) data (cm⁻¹): 2977 (m), 2934 (m), 2903 (m), 1443 (m), 1390 (m), 1273 (m), 1222 (vs), 1205 (s), 1163 (m), 1022 (vs), 938 (m), 813, (m), 775 (m), 587 (m), 517 (m). ¹H NMR (CDCl₃): δ 1.3 (t, 18H, J_{HH} = 7.0 Hz, CH₃/CH₃CH₂-), 4.1 (qd, 12 H, J_{HH} = 7.1 Hz, J_{PH} = 2.7 Hz, CH₂/CH₃CH₂-), 4.5 (s, 2 H, CH₂). ¹³C{¹H} NMR (CDCl₃): δ 68.1 (CH₂), 61.3 (J_{PC} = 5.7 Hz, CH₂/CH₃CH₂-), 16.4 (J_{PC} = 6.3 Hz, CH₃/CH₃CH₂-). ³¹P{¹H} NMR (CDCl₃): δ 126.8.

Synthesis of $\{CH_2(SO_3)_2Ag_2 \cdot [P(OEt)_3]_4\}$ (2g)

Complex **2g** was synthesized following the synthesis of **2a**. In this respect, $[P(OEt)_3]$ (1.4210 g, 8.56 mmol) was reacted with $[CH_2(SO_3)_2Ag_2]$ (0.8343 g, 2.14 mmol). After appropriate work-up (see Section 2.2.1), complex **2e** was obtained as a colourless liquid. Yield: 2.07 g (92%, based on $[CH_2(SO_3)_2Ag_2]$). Anal. Calc. for $C_{25}H_{62}O_{18}Ag_2P_4S_2$: C, 28.48; H, 5.93. Found: C, 28.37; H, 5.82%. IR (KBr) data (cm⁻¹): 2981 (s), 2935 (m), 2904 (m), 1478 (m), 1443 (m), 1391 (m), 1248 (s), 1215 (s), 1208 (s), 1163 (s), 1098 (m), 1019 (vs), 940 (s), 770 (s), 580 (s). ¹H NMR (CDCl₃): δ 1.3 (t, 36 H, J_{HH} = 7.0 Hz, CH₃/CH₃CH₂-), 4.1 (qd, 24 H, J_{HH} = 7.2 Hz, J_{PH} = 1.7 Hz, CH₂/CH₃CH₂-), 4.4 (s, 2 H). ¹³C{¹H} NMR (CDCl₃): δ 68.4 (CH₂), 60.6 (J_{PC} = 4.4 Hz, CH₂/CH₃CH₂-), 16.3 (J_{PC} = 5.5 Hz, CH₃/CH₃CH₂-). ³¹P{¹H} NMR (CDCl₃): δ 128.3.

Synthesis of $\{CH_2(SO_3)_2Ag_2 \cdot [P(OEt)_3]_6\}$ (2h)

Complex **2h** as a colourless liquid was synthesized in the same manner as **2a**. In this respect, $[P(OEt)_3]$ (1.5936 g, 9.60 mmol) was reacted with $[CH_2(SO_3)_2Ag_2]$ (0.6238 g, 1.60 mmol). Yield: 2.02 g (91%, based on $[CH_2(SO_3)_2Ag_2]$). Anal. Calc. for $C_{37}H_{92}O_{24}Ag_2P_6S_2$: C, 32.04; H, 6.69. Found: C, 32.00; H, 6.58%. IR (KBr) data (cm⁻¹): 2982 (vs), 2933 (s), 2905 (m), 1478 (m), 1444 (m), 1391(s), 1244 (s), 1203 (s), 1163 (s), 1098 (m), 1023 (vs), 949 (s), 776 (s), 580 (s). ¹H NMR (CDCl₃): δ 1.3 (t, 54 H, $J_{HH} = 7.0$ Hz, CH_2/CH_3CH_2 -), 4.1 (qd, 36 H, $J_{HH} =$

7.1 Hz, $J_{PH} = 1.3$ Hz, CH_2/CH_3CH_2 -), 4.3 (s, 2 H). ¹³C{¹H} NMR (CDCl₃): δ 68.6 (CH₂), 60.1 ($J_{PC} = 3.3$ Hz, CH_2/CH_3CH_2 -), 16.1 ($J_{PC} = 5.6$ Hz, CH_3/CH_3CH_2 -). ³¹P{¹H} NMR (CDCl₃): δ 130.3.

Structure determination and refinement

Single crystals suitable for X-ray structure measurements of **2c**, **2d** and **2f** were obtained by cooling saturated dichloromethane and toluene solutions containing these complexes to -30 °C. Suitable crystals for X-ray determination were placed in glue under N₂ due to their sensitivities to oxygen and moisture. The X-ray structure measurements were performed on a BRUKER SMART Apex CCD, detector equipped with graphite monochromatic Mo K α radiation ($\lambda = 0.71073$ Å). The structures were solved by direct methods using SHELXS-97.³⁰ The structures were refined by full-matrix least-square procedures on F^2 using SHELXL-97.³¹ All non-hydrogen atoms were refined anisotropically, while the hydrogen atoms were refined using a riding model.[†] The crystallographic data and selected bond distances and angles for **2c**, **2d** and **2f** are listed in Table 1 and Table 2, respectively.

2c. One Cl atom and C atom of the CH_2Cl_2 are disordered and have been refined to split occupancies of 0.363/0.637 (Cl2, C81).

2d. One of the SO_3 groups of the $CH_2(SO_3)_2$ ligand is disordered and has been refined to split occupancies of 0.35/0.65 (S1, O1–O2).

2f. The C atoms in CH₃ groups of two P(OEt)₃ ligands are disordered and have been refined to split occupancies of 0.67/0.33 (O16, C9, C10), 0.67/0.33 (O22, C21, C22) and 0.60/0.40 (O24, C25, C26). One –OCH₂ unit of a P(OEt)₃ ligand is disordered and has been refined to split occupancies of 0.60/0.40 (O24, C25).

Results and discussion

Synthesis and characterization

The organophosphine/phosphite stabilized disilver(I) methanedisulphonates of type $[CH_2(SO_3)_2Ag_2 \cdot L_n]$ (L = PPh₃; n = 2,

2c 2d 2f Bond distances Ag(1) - O(5)2.367(4)Ag(1) - O(5)2.462(3)Ag(1) - P(1)2.328(1) $C(1)-S(2)^{i}$ 1.791(2)Ag(1) - P(2)Ag(1)–O(2) 2.355(2) 2.420(2)Ag(1) - P(5)2.501(1)C(2) - S(3)1.782(3) 2.505(1) Ag(1) - P(1)2.425(2) Ag(1) - P(1)Ag(1) - O(4)2.358(2) C(2)-S(4)1.784(2)Ag(1)-O(2) 2.465(4) Ag(1) - P(2)2.509(1)Ag(1) - O(1)2.375(2)O(1) - S(1)1.446(2) Ag(2) - P(4)2.426(2) Ag(2) - O(3)2.365(3) Ag(2) - O(7)2.300(2)O(2) - S(1)1.457(2) 2.442(2)Ag(2) - P(4)2.333(8) 1.465(2) Ag(2) - P(3)2.437(1)Ag(2) - P(2)O(3) - S(1)2.351(2) 2.461(4)2.437(1)1.448(2)Ag(2) - O(1)Ag(2) - P(3)Ag(2) - O(10)O(4) - S(2)Ag(2) - O(4)2.461(4) Ag(2)–O(6) 2.481(3)Ag(2) - O(3)2.593(2) O(5) - S(2)1.441(2)1.784(7) C(91) - S(2)C(1)-S(1)Ag(3)-O(9) 2.327(2) 1.457(2) 1.787(4)O(6) - S(2)C(1)-S(2)1.793(6) C(91)-S(1)1.796(4) Ag(3) - P(3)2.348(9) O(7) - S(3)1.460(2)O(1)-S(2) O(1) - S(1)1.447(4) 2.374(2)1.436(2) 1.460(4)Ag(3)-O(11) O(8) - S(3)O(2) - S(2)1.459(4) O(2) - S(1)1.599(1)Ag(4) - O(3)2.300(2)O(9) - S(3)1.456(2)1.444(4) O(3) - S(2)O(3) - S(1)1.419(3) Ag(4)-P(4)2.339(1)O(10) - S(4)1.454(3) 2.390(2) O(4) - S(1)1.460(5)O(4) - S(2)1.434(3)Ag(4) - O(6)O(11) - S(4)1.466(2)O(5) - S(1)1.454(4) O(5) - S(2)1.465(3) Ag(4) - O(11)2.526(2)O(12)-S(4) 1.440(2)1.444(5) O(6) - S(1)O(6) - S(2)1.445(3)C(1)-S(1)1.777(2)Bond angles O(5)-Ag(1)-P(2) 112.6(1) O(5)-Ag(1)-P(5) 99.7(8) P(1)-Ag(1)-O(2) 133.5(5) O(9)-Ag(3)-O(11) 80.2(7)111.0(1)O(5) - Ag(1) - P(1)98.8(7) P(1)-Ag(1)-O(4)118.8(6) P(3)-Ag(3)-O(11)137.4(5)O(5) - Ag(1) - P(1)149.5(5) P(5)-Ag(1)-P(1) 109.9(4) 130.3(5) 89.4(7) P(2)-Ag(1)-P(1)O(2)-Ag(1)-O(4) O(3)-Ag(4)-P(4) O(5)-Ag(1)-O(2) 81.7(1) O(5)-Ag(1)-P(2) 122.6(7) P(1)-Ag(1)-O(1) 132.1(5) O(3)-Ag(4)-O(6) 81.8(6) 113.3(4) 83.5(6) P(2)-Ag(1)-O(2) 110.1(1) P(5)-Ag(1)-P(2) P(4)-Ag(4)-O(6) 126.3(5) O(2)-Ag(1)-O(1) P(1)-Ag(1)-O(2)98.7(1) P(1)-Ag(1)-P(2)111.2(4)O(4) - Ag(1) - O(1)83.8(7) O(3)-Ag(4)-O(11) 93.2(6) 109.5(1) P(4)-Ag(2)-P(3)137.4(6) O(3)-Ag(2)-P(4) O(7) - Ag(2) - P(2)140.3(5)P(4)-Ag(4)-O(11) 103.0(6) 108.5(1) P(4)-Ag(2)-O(4)O(3) - Ag(2) - P(3)113.2(1)O(7) - Ag(2) - O(10)83.7(6) O(6) - Ag(4) - O(11)79.0(7)P(3)-Ag(2)-O(4)104.1(1)P(4)-Ag(2)-P(3)127.5(4) P(2)-Ag(2)-O(10)127.5(5)O(9) - Ag(3) - P(3)139.8(5) 105.9(1) 81.5(1) 88.5(6) $S(1)-C(1)-S(2)^{i}$ 117.8(1) P(4)-Ag(2)-O(1)O(3) - Ag(2) - O(6)O(7) - Ag(2) - O(3)105.9(1) P(4)-Ag(2)-O(6) 112.5(9) P(2)-Ag(2)-O(3) 117.8(5) S(3)-C(2)-S(4)117.4(1) P(3)-Ag(2)-O(1) O(4)-Ag(2)-O(1) 80.3(1) P(3)-Ag(2)-O(6) 102.9(8) O(10)-Ag(2)-O(3) 80.1(7) S(1)-C(1)-S(2)117.5(3) S(2)-C(91)-S(1) 120.0(3)

Table 2 Selected bond distances (Å) and angles (°) for complexes 2c, 2d and 2f

Symmetry code: (i) -x, -y + 2, -z.

2a; n = 3, **2b**; n = 4, **2c**; n = 5, **2d**; n = 6, **2e**; $L = P(OEt)_3$; n = 2, **2f**; n = 4, **2g**; n = 6, **2h**) were prepared by the consecutive reaction of [CH₂(SO₃)₂Ag₂] with auxiliary donor ligands in stoichiometry in dichloromethane as solvent at 0 °C (Scheme 1). The complexes were isolated in high yield as white solids (2a-2f) or colorless liquids (2g, 2h), which were stable under an inert atmosphere for months at room temperature. On exposure to air they all decomposed within days (2a-2h) to form brown products.



Scheme 1 Synthesis of complexes 2a-2h.

The complexes also could be prepared by treatment of [AgNO₃] with auxiliary donor ligands and $[CH_2(SO_3)_2K_2]$ in diethyl ether at 0 $^{\circ}$ C (eqn (1)). The disadvantage of the synthesis procedures described in eqn (1) for 2a-2h is the purification because some products may contain traces of chloride which is detrimental to their use as CVD precursors in microtechnology. These preparative studies show that an economical and straightforward synthesis route to prepare organophosphine/phosphite stabilized disilver(I) methanedisulphonate complexes is presented.



Complexes 2a-2h were characterized by elemental analyses, FT-IR, ¹H-, ¹³C{¹H}- and ³¹P{¹H}-NMR spectroscopy (Experimental section). The molecular structures of 2c, 2d and 2f in the solid state are reported.

In the IR spectra, the medium-weak bands at 2977–2981 and 3051–3052 cm⁻¹ are assigned to the aliphatic and aromatic C-H stretch, respectively. As we know, the typical group vibration of sulfonates shows in the range of 1350–1050 cm^{-1} .^{32,33} When the SO₃anion is "free" (non-coordinated), it shows local $C_{3\nu}$ -symmetry with two v_{so} bands for the symmetry. Upon coordination to a metal, the C_{3v} -symmetry is broken and for a C_s -symmetrical – SO₂–O–M moiety and three v_{so} bands are observed ($v^{as}(SO_2)$; $v^s(SO_2)$; v(S-O)). In the IR spectra of **2a–2h**, the SO₃ groups show their characteristic group frequencies. The prominent absorptions in the range of 1222–1250 cm⁻¹ and 1200–1205 cm⁻¹ can be attributed to the asymmetric and symmetric vibration of SO₂.^{34–38} The absorptions around 1090 cm⁻¹ can be assigned as vibration of S–O, which is similar to a previous report.³⁹ Absorption bands of triethylphosphite derived from P–O–C stretching vibrations are shifted for **2f–2h** by 7–11 cm⁻¹ and in comparison with the free triethylphosphite (1030 cm⁻¹), which confirms the coordination of the ligands.⁴⁰

The NMR spectra (¹H, ¹³C{¹H} and ³¹P{¹H}) were recorded for all complexes at room temperature. In ¹H NMR spectra, the integration area ratios are consistent with the stoichiometries of the complexes. The protons of complexes **2a–2e** in the aryl proton region appear in the range of 7.2–7.4 ppm. The complexes (**2f– 2h**) are easily distinguished because the resonances of the protons show only two groups. The protons of $-CH_2$ – in $-O_3SCH_2SO_3$ – appear in the range of 3.9–4.5 ppm as a single signal, which agrees well with a previous report.⁴¹ In the ¹³C{¹H} NMR spectra of **2a–2e**, the triphenylphosphine carbon resonances appear in the range of 128.7–134.1 ppm. The carbon resonances of $-CH_2$ – on $-O_3SCH_2SO_3$ – are observed in the lower field (68.1–68.9 ppm) comparing to that of [P(OEt)₃] (60.1–61.3 ppm).

At room temperature, the phosphorus resonance signals for all coordination complexes **2a–2e** and **2f–2h** appear between 5.0– 11.5 ppm and 126.8–130.3 ppm as single signals, respectively. A trend can be seen in the chemical shift of the ³¹P{¹H} NMR signals for **2f–2h** as a previous report.⁴² Complexes with only one equivalent phosphite ligand per silver(I) centre show a signal at higher field, while addition of a second and a third equivalent of P(OEt)₃ subsequently shifts the signals to lower field, *i.e.* **2f**: 126.8, **2g**: 128.3, and **2h**: 130.3 ppm (Experimental section). The chemical shifts are similar to the observed values for PPh₃ ligands coordinated to silver(I) and can be compared with those of related compounds: $[Ag_2(pz)_2(PPh_3)_2]$ (pz = pyrazole) at δ 9.87,⁴³ $[Ag_4(L_4)(PPh_3)_{10}]$ ·8H₂O (L₄ = 1,3,6,8-pyrenetetrasulfonate) at δ 9.44⁴⁴ and $[Ag_2(pz)_2(PPh_3)_3]$ (pz = pyrazole) at δ 6.13.⁴³

Molecular structures of complexes 2c and 2d-2f

Single crystals of $[CH_2(SO_3)_2Ag_2 \cdot (PPh_3)_4]$ (2c), $[CH_2(SO_3)_2 - CH_2(SO_3)_2]$ $Ag_{2}(PPh_{3})_{5}$ (2d), and $\{CH_{2}(SO_{3})_{2}Ag_{2}(P(OEt)_{3})_{2}\}_{2}$ (2f) could be grown by cooling a saturated dichloromethane and toluene solution containing these species to -30 °C. Complexes 2c and 2f crystallize in the triclinic space group P-1, and 2d crystallizes in the monoclinic space group $P2_1/n$. Because of different molar ratio of triphenylphosphine with disilver(I) methanedisulphonates, complex 2c exhibits an anticipated dinuclear structure of two sixmembered ring systems like cyclic β -diketones, with each silver atom coordinated by two PPh₃ groups. Complex 2d, however, is a dinuclear structure of only one ring system, with one silver atom coordinated by two PPh₃ groups and the other silver atom coordinated by three PPh₃ groups. Important crystal data, collection and refinement parameters are presented in Table 1 (Experimental section). Selected bond distances (Å) and angles (°) of 2c, 2d and 2f are summarized in Table 2.

In the case of **2c**, the asymmetric unit comprises one molecule of **2c**, one molecule of dichloromethane and one molecule of toluene, as shown in Fig. 1. In the structure of **2c**, the $Ag_2S_2O_6$ core of the molecule is regarded as a "Lei Feng hat" framework (Fig. 1 below left), with the crown of the hat occupied by the methanedisulfonic carbon atom and the earflaps occupied by silver atoms and four methanedisulfonic oxygen atoms. Each silver atom is coordinated by two phosphorus atoms of triphenylphosphine and two methanedisulfonic oxygen atoms, thereby completing a distorted tetrahedral coordination arrangement of each silver atom and forming the eight-membered ring (AgOSOAgOSO) (Fig. 1 below right). The angles of P–Ag–P [130.3(5)°, 137.4(6)°] are close to the reported complex [CH₃SO₃Ag·(PPh₃)₂] 132.4(4)°.⁴⁵



Fig. 1 Molecular structure (top), structure of "Lei Feng hat" framework (below left) and (AgOSOAgOSO) skeleton (below right) of **2c**, showing 30% probability displacement ellipsoids. The hydrogen atoms and solvent molecules are omitted for clarity.

Complex 2d is composed of one molecule of 2d and four molecules of dichloromethane, as shown in Fig. 2. Because of the different molar ratio of triphenylphosphine with disilver(I) methanedisulphonates, the eight-membered ring (AgOSOAgOSO) is destroyed, but one six-membered ring (CSOAgOS) remains intact. One silver atom is coordinated by two phosphorus atoms of triphenylphosphine and two methanedisulfonic oxygen atoms, but another silver atom is coordinated by three phosphorus atoms of triphenylphosphine and only one methanedisulfonic oxygen atom at the same time, hence completing a distorted tetrahedral coordination arrangement of each silver atom. The angle of P(3)-Ag(2)-P(4) [127.5(4)°] is a little smaller than that of complex 2c and the reported complex [CH₃SO₃Ag·(PPh₃)₂] [132.4(4)°].⁴⁵ The angles of P-Ag(1)-P[111.2(4)°, 113.3(4)°, 109.9(4)°] are similar to the reported complex [C₄H₄O₂NAg·(PPh₃)₃] [113.3(5)°, 113.7(5)°, 109.5(5)°].⁴⁶

Complex **2f** represents a novel tetramer (Fig. 3), which contains four eight-membered rings (AgOSOAgOSO), which are connected by Ag atoms with sulfonic third O atoms and eight-membered ring



Fig. 2 Molecular structure of 2d, showing 30% probability displacement ellipsoids. The hydrogen atoms and solvent molecules are omitted for clarity.



Fig. 3 Molecular structure of 2f, showing 30% probability displacement ellipsoids. The hydrogen atoms and solvent molecules are omitted for clarity.

O atoms, respectively (Fig. 4). The asymmetric unit comprises two molecules of **2f**, possessing a crystallographically imposed inversion symmetry with the inversion centre in the centroid of the Ag₂O₂ core. Each Ag(1) ion [Ag(1), Ag(2), Ag(4)] possesses a *pseudo*-tetrahedral environment setup by one P atom from the P(OEt)₃ ligand and three O atoms from different methanedisulphonate groups with bond angles ranging from 79.0(7)° to 149.5(5)° except Ag(3). The Ag(1)–O(2) [2.355(2) Å] distance of the Ag₂O₂ core is shorter than other connective bonds Ag(2)–O(3) [2.593(2) Å] and Ag(4)–O(11) [2.526(2) Å], and it is similar to the situation in complex {CH₂(SO₃)₂Ag₂·[P(OMe)₃]₂}_∞ [connective bonds Ag–O: 2.363(3) Å and 2.510(3) Å].⁴⁷

With auxiliary donor ligands, the averaged angles of S–C–S [2c: 117.5(3)°, 2d: 120.0(3)°, 2f: 117.6(1)°] and O–Ag–O [2c: 81.0(1)°, 2d: 81.5(1)°, 2f: 82.3(2)°] in the ring systems (Fig. 1 below right) are larger than those [111.8(4)° and 77.3(2)°] of the reported complex [CH₂(SO₃)₂Ag₂],⁴⁸ but close to the others [116.4(7)° and 81.5(2)°] with no ring in complex [CH₂(SO₃)₂Ag₂],⁴⁸ respectively. In the ring systems, the averaged Ag–O distances in complexes [2c: 2.439(4) Å, 2d: 2.423(3) Å, 2f: 2.347(2) Å] are close to that of complex [CH₂(SO₃)₂Ag₂],⁴⁸ In addition, the averaged Ag–P distances in complexes 2c [2.428(1) Å] and 2f [2.337(5) Å] are shorter than the



Fig. 4 Structure $[CH_2(SO_3)_2Ag_2 \cdot P_2]_4$ skeleton of 2f, showing 30% probability displacement ellipsoids.

sum of covalent radii of the P and Ag atoms $(2.44 \text{ Å})^{49}$ and that [2.478(1) Å] of complex **2d**, they are all shorter than that [2.494(7) Å] of complex $[(R_3P)_2AgPI]$ (PI = $C_8H_4NO_2$).⁵⁰

In general, silver(I) salts of structural type [AgX] (X = organic or inorganic group) contain strongly ionic bonds or are highly aggregated.^{6,48,51} The role of the neutral donor ligand is to ensure a fully saturated coordination environment at the silver atom to prevent aggregation in the solid state and to enhance stability during volatilization.

Disilver(I) methanedisulphonates $[CH_2(SO_3)_2Ag_2]$ with no auxiliary donor ligand are highly aggregated and form a chain structure containing strongly ionic bonds. The metal atom coordination numbers (CN) are 5 and 6 as observed in A (Scheme 2).48 With two auxiliary donor ligands, the special structure of C⁴⁷ exhibits an infinite chain structure of eight-membered rings (AgOSOAgOSO) fully interconnected with O atoms from the sulfonic ligands, where as the tetramer of **B** exhibits a short chain structure of four eightmembered rings (AgOSOAgOSO) whereby the CNs are 3 and 4, respectively. However, the structures with four auxiliary ligands (D) and five auxiliary ligands (E) are typical dinuclear monomers (Scheme 2). With donor ligands $P(P = PPh_3, P(OEt)_3 \text{ or } P(OMe)_3)$, the ring systems of the 2: 2 complex $[CH_2(SO_3)_2Ag_2 \cdot (P)_2]_n$ and the 2: 4 complex $[CH_2(SO_3)_2Ag_2 \cdot (P)_4]$ can remain intact unlike the 2: 5 complex $[CH_2(SO_3)_2Ag_2(P)_5]$. With donor ligands P (P = PPh₃), half of the ring system in the 2:5 complex $[CH_2(SO_3)_2Ag_2 \cdot (P)_5]$ is destroyed with the CN of the metal atoms 4 as in E. Common for type C-E molecules is that the silver(I) ion possesses a tetrahedral surrounding, with 18-valence electrons. Only large ligands and the numbers of auxiliary donor ligands may prevent molecules containing strong ionic bonds and forming oligomers.

TG and MOCVD studies

TG and DSC studies are required to optimize the temperature at which the respective single silver precursor should be maintained during the MOCVD experiments. For example, the TG and DSC curves of complex **2g** are shown in Fig. 5. It can be seen from the DSC curve that there is one apparent endothermic process from 92 °C to 426 °C with a small peak in temperature at 225 °C and 324 °C. Firstly, it may illustrate dissociation of three triethylphosphite ligands between 94 °C and 228 °C with corresponding weight loss of about 47.98% which is close to the theoretical loss (47.28%). Then, the weight loss between 228 °C



Scheme 2 Schematic representation of structural type A-E molecules.



Fig. 5 TG and DSC curves of 2g (heating rate 10 °C min⁻¹, argon atmosphere).

and 233 °C is the result of the elimination of the 4th P(OEt)₃ ligand with corresponding weight loss of about 14.86% which is close to the theoretical loss (15.76%). It is very difficult to know the real thermal decomposition mechanism of methanedisulphonates from 233 to 395 °C. The final percentage of the residue is 20.85%, which is close to the theoretical value of silver (20.46%). The thermal measurement is in good agreement with the structural analysis.

Complexes 2a-2f were solid state with a lower volatility than complexes 2g and 2h. It is difficult to make the precursor vapor and transport into the reacting zone of the CVD reactor. In addition, according to the thermal properties obtained from the TG and DSC studies, the disilver complexes decompose with release of the auxiliary ligands first. Therefore, on the basis of the properties of complexes 2a-2h, we choose 2g as a potential CVD precursor to grow silver films first.

The deposition of silver films were conducted using a vertical quartz tube hot-wall MOCVD reactor at temperatures between 395 °C and 450 °C. Oxidized silicon as substrates were applied and the typical deposition time was limited to 60 min. For each MOCVD experiment, approximately 500 mg of 2g was

charged into the sample reservoir, maintained at 85 °C to ensure the generation of adequate partial pressure of the sample. A stream of nitrogen was introduced with the flow rate adjusted to 30 sccm under a pressure of 6×10^{-5} bar. The surface morphology and composition of the silver films from the MOCVD experiments using 2g were examined by SEM and EDX analysis (Fig. 6).

Their morphologies exhibit obvious differences depending on their deposition temperature. At 395 °C, the film is not completely closed and homogeneous and is composed of two kinds of particulates spread all over the substrate surface. From our analytical data, it can be seen that the film deposited at 395 °C is a grayish-white color and exhibits the highest level of impurities. However, the silver metal coverage became significantly better as the deposition temperature was increased to 420 °C. The dense and homogeneous silver layer is composed of many well isolated, granular particulates spread all over the substrate surface. The sizes of silver grains are in the range of 50-70 nm. Finally, upon further increase of the deposited temperature to 450 °C, the quality of the metal coverage was poor. This observation is consistent with the fact that the nuclear growth rate of the silver deposit is much greater than that of the formation of the initial nucleation sites on the substrate, which then gives much larger metal aggregation instead of giving better thin film uniformity.47 EDX analyses of the as-deposited films at 420 °C and 450 °C show the presence of silver alone. The other light elements, such as C, and P, which might be present as impurities or formed by surface oxidation of silver, are below the detection limit. The average film thickness at different temperature were about 0.53 µm, 0.62 µm, 0.77 µm, respectively.

The UV-Vis absorption spectra of the silver films deposited at 395 °C, 420 °C and 450 °C are shown in Fig. 7. The absorption spectra of the as-deposited film at 395 °C shows a broad peak at 400 nm. The absorption of the as-deposited films at 420 °C and 450 °C are red shifted towards 416 nm and 412 nm, respectively. The absorption peaks at ca. 405 nm are due to the surface plasmon polariton resonance (SPPR) of Ag particles, which are sensitive to the microstructure of the films.52 The peak broadness is due to dipole-dipole interactions of the Ag particles.53-55



Fig. 6 SEM images and EDX spectrums of the films deposited from 2g using N₂ as the carrier gas at temperatures (a) 395 °C, (b) 420 °C, (c) 450 °C.



Fig. 7 UV–Vis spectra of the films deposited from 2g using N₂ as the carrier gas at temperatures (A) 395 °C, (B) 420 °C, (C) 450 °C.

Conclusions

A straightforward synthesis methodology for the preparation of a series of organophosphine/phosphite disilver(1) methanedisulphonates complexes of composition $[CH_2(SO_3)_2Ag_2$. $L_n]$ (L = PPh₃, P(OEt)₃; n = 2, 3, 4, 5, 6) is described. The solid state structures of three metal–organic complexes were determined by single X-ray structure analysis. It was found that depending on the number (*n*) and the size of the auxiliary ligands in complexes $[CH_2(SO_3)_2Ag_2 \cdot L_n]$ different structural motifs were obtained. Complex **2g** was used as a precursor in the deposition of silver for the first time by using the MOCVD technique. The as-deposited film at 420 °C is dense and homogeneous, which is composed of many well isolated, granular particulates spread all over the substrate surface. The EDX results showed that the

obtained layer is composed of pure silver within the detection limit of EDX.

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Notes and references

- 1 T. T. Kodas, M. J. Hampden-Smith, in *The Chemistry of Metal CVD*, VCH, Weinheim, Germany, 1994.
- 2 P. Piszczek, E. Sylyk, M. Chaberski, C. Taeschner, A. Leonhardt, W. Bala and K. Bartkiewicz, *Chem. Vap. Deposition*, 2005, **11**, 53–59.
- 3 H. Schmidt, Y. Shen, M. Leschke, T. Haase, K. Kohse-Höinghaus and H. Lang, J. Organomet. Chem., 2003, 669, 25–31.
- 4 E. S. Robin, W. T. David and F. St. C. Anne, *Chem. Mater.*, 1997, 9, 501–510.
- 5 J. Fraden, in *Handbook of modern sensors: physics, design and applications*, 2nd edn American Institute of Physics, 1997.
- 6 A. Jakob, H. Schmidt, P. Djiele, Y. Z. Shen and H. Lang, *Microchim. Acta*, 2007, **156**, 77–81.
- 7 Y. F. Lu, M. Takai, S. Nagatomo, K. Kato and S. Namba, *Appl. Phys.* A: Solids Surf., 1992, **54**, 51–56.
- 8 H. Liedberg and T. Lundeberg, Urol. Res., 1989, 17, 359-360.
- 9 M. Hauder, W. Hansch, J. Gstootner and D. Schmitt-Landsiedel, Appl. Phys. Lett., 2001, 78, 838–840.
- 10 J. Uchil, K. Mohan Rao and M. Pattabi, J. Phys. D: Appl. Phys., 1996, 29, 2992–2996.
- 11 A. C. Carter, W. Chang, S. B. Qadri, J. S. Horwitz, R. Leuchtner and D. B. Chrisey, J. Mater. Res., 1998, 13, 1418–1421.
- 12 A. Grodzicki, I. Lakomska, P. Piszczek, I. Szymanska and E. Szlyk, Coord. Chem. Rev., 2005, 249, 2232–2258.
- 13 A. Jain, K. Chi, T. T. Kodas and M. J. Hampden-Smith, J. Electrochem. Soc., 1993, 140, 1434–1439.
- 14 N. Awaya, Y. Arita, Proceedings of the 1991 Symposium on VLSI Thchnology, Orso, Japan, 1991, p. 37.

- 16 G. Braeckelmann, D. Manger, A. Burke, G. G. Peterson, A. E. Kaloyeros, C. Reidsema, T. R. Omstead, J. F. Loan and J. J. Sullivan, J. Vac. Sci. Technol., 1996, B14, 1828–1836.
- 17 S. Kim, D. J. Choi, K. R. Yoon, K. H. Kim and S. K. Koh, *Thin Solid Films*, 1997, **311**, 218–221.
- 18 R. J. H. Voorhoeve and J. W. Merewether, J. Electrochem. Soc., 1972, 119, 364–368.
- 19 C. Oehr and H. Suhr, Appl. Phys. A: Solids Surf., 1989, 49, 691-696.
- 20 M. J. Shapiro, W. J. Lackey, J. A. Hanigofsky, D. N. Hill, W. B. Carter and E. K. Barefield, J. Alloys Compd., 1992, 187, 331–349.
- 21 P. M. Jeffries, S. R. Wilson and G. S. Girolami, J. Organomet. Chem., 1993, 449, 203–209.
- 22 N. H. Dryden, J. J. Vittal and R. J. Puddephatt, *Chem. Mater.*, 1993, 5, 765–766.
- 23 Z. Yuan, N. H. Dryden, J. J. Vittal and R. J. Puddephatt, *Chem. Mater.*, 1995, 7, 1696–1702.
- 24 D. A. Edwards, R. M. Harker, M. F. Mahon and K. C. Molloy, J. Mater. Chem., 1999, 9, 1771–1780.
- 25 W. Lin, T. H. Warren, R. G. Nuzzo and G. S. Girolami, J. Am. Chem. Soc., 1993, 115, 11644–11645.
- 26 S. Serghini-Monim, Z. Yuan, K. Griffiths, P. R. Norton and R. J. Puddephatt, J. Am. Chem. Soc., 1995, 117, 4030–4036.
- 27 Z. Yuan, N. H. Dryden, X. Li, J. J. Vittal and R. J. Puddephatt, J. Mater. Chem., 1995, 5, 303–307.
- 28 D. A. Edwards, R. M. Harker, M. F. Mahon and K. C. Molloy, *Inorg. Chim. Acta*, 2002, **328**, 134–146.
- 29 K. Anastas, Acta Crystallogr., Sect. B: Struct. Crystallogr. Cryst. Chem., 1981, B37, 2232–2234.
- 30 G. M. Sheldrick, Acta Crystallogr., Sect. A: Found. Crystallogr., 1990, 46, 467–473.
- 31 G. M. Sheldrick, SHELXL-97, Program for Crystal Structure Refinement, University of Göttingen, 1997.
- 32 L. J. Bellamy, *The Infrared Spectra of Complexes Moleculaes*, Vol. 1, Chapman and Hall, London, third ed., 1975.
- 33 M. G. Miles, G. Doyle, R. P. Cooney and R. S. Tobias, Spectrochim. Acta, Part A, 1969, 25, 1515–1526.

- 34 R. J. Capwell, K. H. Rhee and K. S. Seshadri, *Spectrochim. Acta, Part A*, 1968, 24, 955–958.
- 35 S. M. Chackalackal and F. E. Stafford, J. Am. Chem. Soc., 1966, 88, 4815–4819.
- 36 R. Bala, R. P. Sharma and A. D. Bond, J. Mol. Struct., 2007, 830, 198–203.
- 37 C. Y. Panicker, H. T. Varghese, D. Philip and H. I. S. Nogueira, Spectrochim. Acta, Part A, 2006, 64, 744–747.
- 38 D. Philip, A. Eapen and G. Aruldhas, J. Solid State Chem., 1995, 116, 217–223.
- 39 D. Jamro and Y. Marechal, J. Phys. Chem. B, 2005, 109, 19664–19675.
- 40 L. W. Daasch and D. C. Smith, Anal. Chem., 1951, 23, 853-868.
- 42 R. Mothes, T. Rüffer, Y. Z. Shen, A. Jakob, B. Walfort, H. Petzold, S. E. Schulz, R. Ecke, T. Gessner and H. Lang, J. Chem. Soc., Dalton Trans., 2010, 39, 11235–11247.
- 43 G. A. Ardizzoia, G. La Monica, A. Maspero, M. Moret and N. Masciocchi, *Inorg. Chem.*, 1997, 36, 2321–2328.
- 44 F. F. Li, J. F. Ma, J. Yang, H. Q. Jia and N. H. Hu, J. Mol. Struct., 2006, 787, 106–112.
- 45 Y. Y. Zhang, Y. Wang, X. Tao, N. Wang and Y. Z. Shen, *Polyhedron*, 2008, 27, 2501–2505.
- 46 X. Tao, Y. Q. Li, H. H. Xu, N. Wang, F. L. Du and Y. Z. Shen, *Polyhedron*, 2009, 28, 1191–1195.
- 47 X. Tao, K. C. Shen, M. Feng, Q. Y. Tang, J. T. Fang, Y. L. Wang and Y. Z. Shen, *Polyhedron*, 2011, in press.
- 48 P. F. Charbonnier and R. F. H. Loiseleur, Acta Crystallogr., Sect. B: Struct. Crystallogr. Cryst. Chem., 1979, B35, 1773–1775.
- 49 B. K. Teo and J. C. Calabrese, Inorg. Chem., 1976, 15, 2467-2758
- 50 D. R. Whitcomb and M. Rajeswaran, J. Chem. Crystallogr., 2006, 36, 587–598.
- 51 H. Schmidt, Y. Shen, M. Leschke, T. Haase, K. Kohse-Höinghaus and H. Lang, J. Organomet. Chem., 2003, 669, 25–31.
- 52 D. D. Evanoff, Jr. and G. Chumanov, *ChemPhysChem*, 2005, **6**, 1221–1231.
- 53 T. W. Ebbesen, H. J. Lezec, H. F. Ghaemi, T. Thio and P. A. Wolff, *Nature*, 1998, **391**, 667–669.
- 54 S. Link and M. A. El-Sayed, J. Phys. Chem. B, 1999, 103, 8410-8426.
- 55 D. D. Evanoff, Jr. and G. Chumanov, J. Phys. Chem. B, 2004, 108, 13957–13962.