

Mono- and bimetallic silver(I) complexes with bridging and terminal-bound organic chelating ligands

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Dedicated to Professor Pierre Braunstein.

Abstract

The synthesis of the mononuclear and homobimetallic silver(I) complexes $[\text{P}(\text{C}_6\text{H}_4\text{CH}_2\text{NMe}_2)_3]\text{AgL}_2$ [$\text{L}_2 =$ acetylacetonate, acac (**5a**); tropolonate, trop (**5b**); 3-hydroxy-2-methyl- γ -pyranoate, pyro (**5c**)], $[\text{P}(\text{C}_6\text{H}_4\text{CH}_2\text{NMe}_2)_3]\text{AgOC}(\text{O})\text{Me}$ (**8**) and $[\text{P}(\text{C}_6\text{H}_4\text{CH}_2\text{NMe}_2)_3]\text{Ag-L}_4\text{-Ag}[\text{P}(\text{C}_6\text{H}_4\text{CH}_2\text{NMe}_2)_3]$ [$\text{L}_4 =$ 2,5-dihydroxy-*p*-benzochinoate, benz (**6a**); 1,4-dihydroxy-anthra-chinoate, anthra (**6b**)] can be achieved by the reaction of the silver(I) salts $[\text{AgL}_2]$ [$\text{L}_2 =$ acac (**3a**), trop (**3b**), pyro (**3c**)], $[\text{Ag}_2\text{L}_4]$ [$\text{L}_4 =$ benz (**3d**), anthra (**3e**)] or $[\text{AgCO}_2\text{Me}]$ (**7**) with $\text{P}(\text{C}_6\text{H}_4\text{CH}_2\text{NMe}_2)_3$ (**4**) in a 1:1 or 1:2 molar ratio. The respective silver(I) salts **3a–3e** are accessible by treatment of $[\text{AgNO}_3]$ (**1**) with HL_2 or H_2L_4 (**2a–2d**), respectively. In **5a–5c**, **6a** and **6b** the silver atom possesses a pseudotetrahedral environment caused by the chelate-bound ligands acac, trop, pyro, benz or anthra and the bidentate coordinated phosphane **4**. In homobimetallic **6a** and **6b** the appropriate transition metals are spanned by the benz or anthra units, respectively. While in **5a–5c**, **6a** and **6b** the silver metal possesses the coordination number 4, in **8** a T-shaped arrangement is set-up with a linear P–Ag–O unit. The chemical and physical behaviour of complexes **5a–5c**, **6a**, **6b** and **8** is reported. Spectroscopic studies reveal that on the NMR time-scale the phosphane group with its Me_2NCH_2 built-in arms is dynamic.

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1. Introduction

Recently, it could be shown that the hypervalent triaryl-phosphane $\text{P}(\text{C}_6\text{H}_4\text{CH}_2\text{NMe}_2)_3$ enables the successful synthesis of diverse copper(I) and copper(II) species with copper in different coordination spheres [1,2]. In the solid-state, the structure of these complexes is dominated by the coordination number 3 (trigonal-planar), 4 (distorted tetrahedral or square-pyramidal) or 5 (trigonal-bipyramidal) of the copper atom [1,2]. Besides such mononuclear copper(I) complexes [1] a new type of a dicopper structure, $[\text{P}(\text{C}_6\text{H}_4\text{CH}_2\text{NMe}_2-$

$)]_2\text{Cu}(\mu\text{-X})\text{CuX}$ ($\text{X} = \text{Cl}, \text{Br}$), could be prepared in which one copper atom possesses a distorted trigonal-bipyramidal environment, while the other one is almost square-pyramidal coordinated [3]. In the latter homobimetallic transition metal complex a contact ion pair between Cu^+ and CuX_2^- exists [3].

These mono- and bimetallic low-aggregated copper(I) species play an important role, as, for example, catalysts in organic and organometallic synthesis as well as model compounds to study intramolecular electron transfer processes [1–5].

In view of our earlier studies in this area, we report here on the synthesis of silver(I) transition metal complexes, based on oxygen containing mono-, bi- and tetradentate organic ligands and the phosphane $\text{P}(\text{C}_6\text{H}_4\text{CH}_2\text{NMe}_2)_3$ as multidentate ligand.

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2. Experimental

2.1. General methods

All reactions were carried out under an atmosphere of purified nitrogen (O₂ traces: Cu catalyst, BASF AG, Ludwigshafen; H₂O: molecular sieve 4 Å) using standard Schlenk techniques. Tetrahydrofuran, diethyl ether and *n*-pentane were purified by distillation from sodium–benzophenone ketyl; dichloromethane was purified by distillation from P₂O₅. Infrared spectra were recorded on a Perkin–Elmer FT-IR 1000 spectrometer. ¹H NMR were recorded on a Bruker Avance 250 spectrometer operating at 250.130 MHz or on a Bruker AC 200 spectrometer operating at 200.13 MHz in the Fourier transform mode; ¹³C {¹H} NMR spectra were recorded at 62.895 MHz or at 50.323 MHz. Chemical shifts are reported in δ units (parts per million) downfield from tetramethylsilane with the solvent as the reference signal (CDCl₃: ¹H NMR, δ = 7.26; ¹³C {¹H} NMR, δ = 77.0). ³¹P {¹H} NMR were recorded at 101.255 MHz or at 81.015 MHz in CDCl₃ with P(OMe)₃ (δ = 139.0 ppm) as external reference relative to H₃PO₄ (δ = 0.0 ppm). Melting points were determined using sealed capillaries on a Büchi MP 510 melting point (m.p.) apparatus. Microanalyses were performed by the Department of Organic Chemistry at Chemnitz, University of Technology or the Institute of Organic Chemistry, University of Heidelberg, Heidelberg.

Commercial available [AgNO₃] (**1**), 3-hydroxy-2-methyl-γ-pyrone (H-pyro) (**2c**), 2,5-dihydroxy-*p*-benzochinone (H-benz) (**2d**), 1,4-dihydroxyanthrachinone (H-anthra) (**2e**) and [AgCO₂Me] (**7**) were used without further purification. P(C₆H₄CH₂NMe₂-2)₃ (**4**) [6], [Aga-cac] (**3a**) [7] and [Agtrop] (**3b**) [9] were prepared according to literature procedures.

2.2. Synthesis of **3c**

[AgNO₃] (**1**) (0.6 g, 3.53 mmol) was dissolved in acetonitrile (2 ml) and ethanol (50 ml). To this solution 0.445 g (3.53 mmol) of 3-hydroxy-2-methyl-γ-pyrone (**2c**) dissolved in triethylamine (0.5 ml, 0.36 g) and 30 ml of ethanol is added dropwise in the dark at 25 °C. After 2 h of stirring the white precipitate NEt₃⁺NO₃⁻ was separated by filtration and washed three times with 10 ml portions of cold ethanol. All volatiles were removed from the filtrate in oil-pump vacuo leaving the silver(I) salt **3c** as a colourless solid, which gradually darkens on exposure to light. Yield: 0.8 g (3.43 mmol, 97% based on **1**).

M.p.: 165 °C (dec.). IR (KBr) (cm⁻¹): ν_{CO}(asym) = 1624 (vs), ν_{CO}(sym) = 1581 (s). *Anal.* Calc. for C₆H₅AgO₃ (232.970): C, 30.93; H, 2.16. Found: C, 30.49; H, 2.08%.

2.3. Synthesis of **3d** and **3e**

Experimental conditions and work-up were identical to the preparation of **3c**. Experimental details: Synthesis of **3d**: 1.2 g (7.1 mmol) of [AgNO₃] (**1**), 0.49 g (3.5 mmol) of 2,5-dihydroxy-*p*-benzochinone (**2d**) and 1 ml (0.72 g) of NEt₃. Synthesis of **3e**: 1.2 g (7.1 mmol) of [AgNO₃] (**1**), 0.84 g (3.5 mmol) of 1,4-dihydroxy-anthrachinone (**2e**) and 1 ml (0.72 g) of NEt₃.

After appropriate work-up, **3d** and **3e** could be isolated as brown solids.

2.3.1. Compound **3d**

Yield: 1.2 g (3.39 mmol, 96% based on **1**). M.p.: 132 °C (dec.). IR (KBr) (cm⁻¹): ν_{CO} = 1531 (vs). *Anal.* Calc. for C₆H₂Ag₂O₄ (353.812): C, 20.37; H, 0.57. Found: C, 20.05; H, 0.52%.

2.3.2. Compound **3e**

Yield: 1.55 g (3.41 mmol, 96% based on **1**). M.p.: 122 °C (dec.). IR (KBr) (cm⁻¹): ν_{CO}(asym) = 1577 (vs), ν_{CO}(sym) = 1446 (s). *Anal.* Calc. for C₁₄H₆Ag₂O₄ (453.928): C, 37.04; H, 1.33. Found: C, 36.79; H, 1.20%.

2.4. Synthesis of mononuclear **5a–5c**

To 400 mg (0.92 mmol) of P(C₆H₄CH₂NMe₂-2)₃ (**4**) dissolved in 50 ml of tetrahydrofuran equimolar amounts of the silver(I) salts **3a–3c** (**3a**: 190 mg; **3b**: 210 mg; **3c**: 215 mg) were added in one portion in the dark at 25 °C. After 2 h of stirring at this temperature the reaction mixture was filtrated through a pad of Celite. All volatiles were removed in oil-pump vacuo and the remaining yellow to brown solids were washed three times with 10 ml portions of *n*-pentane. Complexes **5a–5c** were obtained as brown (**5a**) or pale yellow (**5b**, **5c**) solids, which gradually darken on exposure to light.

2.4.1. Compound **5a**

Yield: 550 mg (0.86 mmol, 93% based on **4**). M.p.: 129 °C (dec.). ¹H NMR (200.13 MHz, CDCl₃): δ = 1.88 (s, 6 H, CH₃/acac), 2.10 (s, 18 H, CH₃/NMe₂), 3.74 (bs, 6 H, CH₂), 5.12 (s, 1 H, CH/acac), 6.83 (pt, *J*_{HH} = 7.7 Hz, 3 H, C₆H₄), 7.1–7.5 (m, 9 H, C₆H₄). ¹³C {¹H} NMR (50.323 MHz, CDCl₃): δ = 29.6 (CH₃/acac), 45.2 (CH₃/NMe₂), 63.2 (d, ³*J*_{PC} = 67.0 Hz, CH₂), 94.8 (CH/acac), 127.1 (d, ³*J*_{PC} = 5.0 Hz, C₆H₄), 129.4 (C₆H₄), 130.9 (C₆H₄), 131.8 (d, ¹*J*_{PC} = 36.9 Hz, ¹C/C₆H₄), 133.6 (C₆H₄), 143.0 (C₆H₄), 189.9 (CO/acac). ³¹P {¹H} NMR (80.015 MHz, CDCl₃): δ = -26.9 (d, ¹*J*_{107Ag,31P} = 626 Hz, ¹*J*_{109Ag,31P} = 727 Hz). *Anal.* Calc. for C₃₂H₄₃AgN₃O₂P (640.523): C, 60.00; H, 6.77; N, 6.56. Found: C, 60.96; H, 7.13; N, 6.66%; please notice, due to rapid decomposition no satisfactory elemental analysis could be obtained.

2.4.2. Compound 5b

Yield: 560 mg (0.85 mmol, 92% based on **4**). M.p.: 110 °C (dec.). IR (KBr) (cm⁻¹): $\nu_{\text{CO}}(\text{asym}) = 1503$ (vs), $\nu_{\text{CO}}(\text{sym}) = 1427$ (s). ¹H NMR (200.13 MHz, CDCl₃): $\delta = 2.05$ (s, 18 H, CH₃), 3.78 (s, 6 H, CH₂), 6.88 (pt, $J_{\text{HH}} = 7.9$ Hz, 3 H, C₆H₄), 7.1–7.4 (m, 14 H, C₆H₄/trop). ¹³C{¹H} NMR (50.323 MHz, CDCl₃): $\delta = 45.9$ (CH₃), 63.5 (d, ³J_{PC} = 13.0 Hz, CH₂), 119.9 (trop), 123.6 (trop), 127.3 (d, ³J_{PC} = 5.6 Hz, C₆H₄), 129.6 (C₆H₄), 131.3 (d, ²J_{PC} = 9.4 Hz, C₆H₄), 132.2 (d, ¹J_{PC} = 26.8 Hz, ¹C/C₆H₄), 133.9 (C₆H₄), 135.6 (trop), 142.8 (d, ²J_{PC} = 15.6 Hz, C₆H₄), 181.0 (CO/trop). ³¹P{¹H} NMR (80.015 MHz, CDCl₃): $\delta = -26.9$ (d, ¹J_{107Ag31P} = 641 Hz, ¹J_{109Ag31P} = 737 Hz). Anal. Calc. for C₃₄H₄₁AgN₃O₂P (662.527): C, 61.63; H, 6.24; N, 6.34. Found: C, 61.61; H, 6.78; N, 6.43%.

2.4.3. Compound 5c

Yield: 580 mg (0.87 mmol, 95% based on **4**). M.p.: 82 °C (dec.). IR (KBr) (cm⁻¹): $\nu_{\text{CO}}(\text{asym}) = 1619$ (vs), $\nu_{\text{CO}}(\text{sym}) = 1452$ (s). ¹H NMR (250.130 MHz, CDCl₃): $\delta = 2.20$ (s, 18 H, CH₃/NMe₂), 2.35 (s, 3 H, CH₃/pyro), 3.57 (bs, 3 H, CH₂), 3.67 (bs, 3 H, CH₂), 6.40 (d, ³J_{HH} = 5.5 Hz, 1 H, pyro), 6.85 (pt, $J_{\text{HH}} = 7.9$ Hz, 3 H, C₆H₄), 7.3–7.5 (m, 9 H, C₆H₄), 7.70 (d, ³J_{HH} = 5.5 Hz, 1 H, pyro). ¹³C{¹H} NMR (62.895 MHz, CDCl₃): $\delta = 14.6$ (CH₃/pyro) 45.1 (CH₃/NMe₂), 64.1 (d, ³J_{PC} = 9.6 Hz, CH₂), 113.6 (pyro), 128.3 (d, ³J_{PC} = 5.6 Hz, C₆H₄), 129.9 (C₆H₄), 131.0 (d, ²J_{PC} = 8.6 Hz, C₆H₄), 132.4 (d, ¹J_{PC} = 17.8 Hz, ¹C/C₆H₄), 133.4 (C₆H₄), 142.1 (d, ²J_{PC} = 12.4 Hz, C₆H₄), 143.7 (pyro), 149.1 (pyro), 153.7 (pyro), 171.2 (CO/pyro). ³¹P{¹H} NMR (101.255 MHz, CDCl₃): $\delta = -29.6$ (d, ¹J_{107Ag31P} = 566 Hz, ¹J_{109Ag31P} = 640 Hz). Anal. Calc. for C₃₃H₄₁AgN₃O₃P (666.516): C, 59.46; H, 6.20; N, 6.31. Found: C, 59.35; H, 6.26; N, 6.31%.

2.5. Synthesis of 6a and 6b

To 400 mg (0.92 mmol) of P(C₆H₄CH₂NMe₂-2)₃ (**4**) dissolved in 50 ml of tetrahydrofuran the silver(I) salts **3d** or **3e**, respectively, were added in one portion in a molar ratio of 2:1 (**3d**: 160 mg, 0.46 mmol; **3e**: 210 mg, 0.46 mmol) in the dark at 25 °C. After 3 h of refluxing, the red solution was filtrated through a pad of Celite and all volatiles were removed in oil-pump vacuo. The thus obtained solids were washed three times with 10 ml portions of *n*-pentane to give **6a** and **6b** as red solids.

2.5.1. Compound 6a

Yield: 520 mg (0.43 mmol, 93% based on **4**). M.p.: 163 °C (dec.). IR (KBr) (cm⁻¹): $\nu_{\text{CO}} = 1525$ (vs). ¹H NMR (250.130 MHz, CDCl₃): $\delta = 2.20$ (s, 36 H, CH₃/NMe₂), 3.38 (bs, 6 H, CH₂), 3.65 (bs, 6 H, CH₂), 6.15 (s, 2 H, benz), 6.85 (pt, $J_{\text{HH}} = 7.8$ Hz, 6 H, C₆H₄), 7.2–7.5 (m, 18 H, C₆H₄). ¹³C{¹H} NMR (62.895 MHz, CDCl₃):

$\delta = 44.6$ (CH₃/NMe₂), 62.6 (d, ³J_{PC} = 14.9 Hz, CH₂), 99.5 (benz), 126.4 (d, ³J_{PC} = 5.0 Hz, C₆H₄), 128.6 (C₆H₄), 130.4 (d, ²J_{PC} = 7.7 Hz, C₆H₄), 131.2 (d, ¹J_{PC} = 26.2 Hz, ¹C/C₆H₄), 132.9 (C₆H₄), 141.8 (d, ²J_{PC} = 16.3 Hz, C₆H₄), 179.1 (CO/benz). ³¹P{¹H} NMR (101.255 MHz, CDCl₃): $\delta = -29.5$ (d, ¹J_{107Ag31P} = 549 Hz, ¹J_{109Ag31P} = 634 Hz). Anal. Calc. for C₆₀H₇₄Ag₂N₆O₄P₂ (1220.91): C, 59.02; H, 6.11; N, 6.88. Found: C, 58.89; H, 6.02; N, 6.95%.

2.5.2. Compound 6b

Yield: 570 mg (0.43 mmol, 94% based on **4**). M.p.: 84 °C (dec.). IR (KBr) (cm⁻¹): $\nu_{\text{CO}}(\text{asym}) = 1629$ (vs), $\nu_{\text{CO}}(\text{sym}) = 1451$ (s). ¹H NMR (250.130 MHz, CDCl₃): $\delta = 2.10$ (s, 36 H, CH₃/NMe₂), 3.59 (bs, 12 H, CH₂), 6.85 (pt, $J_{\text{HH}} = 8.0$ Hz, 6 H, C₆H₄), 7.3–7.4 (m, 18 H, C₆H₄), 7.5 (m, 2 H, anthra), 7.85 (m, 2 H, anthra), 8.35 (s, 2 H, anthra). ¹³C{¹H} NMR (62.895 MHz, CDCl₃): $\delta = 45.1$ (CH₃/NMe₂), 61.7 (d, ³J_{PC} = 21.1 Hz, CH₂), 112.7 (anthra), 126.6 (C₆H₄), 128.1 (C₆H₄), 129.1 (d, ¹J_{PC} = 37.7 Hz, ¹C/C₆H₄), 133.3 (C₆H₄), 134.1 (C₆H₄), 134.4 (anthra), 136.8 (anthra), 137.0 (anthra), 143.3 (d, ²J_{PC} = 22.6 Hz, C₆H₄), 157.7 (anthra), 186.8 (CO/anthra). ³¹P{¹H} NMR (101.255 MHz, CDCl₃): $\delta = -29.1$ (d, ¹J_{107Ag31P} = 562 Hz, ¹J_{109Ag31P} = 641 Hz). Anal. Calc. for C₆₈H₇₈Ag₂N₆O₄P₂ (1321.022): C, 61.82; H, 5.95; N, 6.36. Found: C, 62.01; H, 5.86; N, 6.29%.

2.6. Synthesis of 8

Experimental conditions and work-up are identical to those for the preparation of **5**. In this respect 400 mg (0.92 mmol) of P(C₆H₄CH₂NMe₂-2)₃ (**4**) were reacted with 155 mg (0.92 mmol) of [AgCO₂Me] (**7**). After appropriate work-up complex **8** could be isolated as a very light-sensitive, brown solid. Yield: 510 mg (0.85 mmol, 93% based on **4**).

M.p.: 121 °C (dec.). IR (KBr) (cm⁻¹): $\nu_{\text{CO}} = 1570$ (vs), $\nu_{\text{CO}} = 1393$ (s). ¹H NMR (200.13 MHz, CDCl₃): $\delta = 2.07$ (s, 18 H, CH₃/NMe₂), 2.18 (s, 3 H, CH₃/CO₂Me), 3.51 (d, ²J_{HH} = 8.8 Hz, 3 H, CH₂), 3.77 (d, ²J_{HH} = 8.8 Hz, 3 H, CH₂), 6.85 (pt, $J_{\text{HH}} = 7.1$ Hz, 3 H, C₆H₄), 7.1–7.4 (m, 9 H, C₆H₄). ¹³C{¹H} NMR (50.323 MHz, CDCl₃): $\delta = 23.2$ (CH₃/CO₂Me), 45.6 (CH₃/NMe₂), 64.4 (d, ³J_{PC} = 10.2 Hz, CH₂), 127.5 (d, ³J_{PC} = 4.6 Hz, C₆H₄), 129.5 (C₆H₄), 131.9 (d, ²J_{PC} = 8.3 Hz, C₆H₄), 132.6 (d, ¹J_{PC} = 27.8 Hz, C₆H₄), 134.2 (d, ³J_{PC} = 3.7 Hz, C₆H₄), 142.3 (d, ²J_{PC} = 17.5 Hz, C₆H₄), 177.8 (CO/CO₂Me). ³¹P{¹H} NMR (80.015 MHz, CDCl₃): $\delta = -26.2$ (d, ¹J_{107Ag31P} = 610 Hz, ¹J_{109Ag31P} = 707 Hz). Anal. Calc. for C₂₉H₃₉AgN₃O₂P (600.49): C, 58.01; H, 6.55; N, 7.00. Found: C, 58.13; H, 6.76; N, 6.88%.}}

3. Results

Phosphane-stabilised organo silver(I) complexes of type XAgR (X = Lewis-base, R = organic group) can be prepared by following synthetic strategies: the reaction of XAgNO₃ with CH-acidic substrates, or treatment of [AgNO₃] with R⁻ and then with X [8]. It appeared that the latter reaction is the most favoured one and hence, we used this method in the synthesis of the title complexes **5**, **6** and **8**.

The, therefore, necessary silver(I) salts [AgL₂] [L₂ = acetylacetonate, acac (**3a**); [7] tropolonate, trop (**3b**); 3-hydroxy-2-methyl-γ-pyranoate, pyro (**3c**)] and [Ag₂L₄] [L₄ = 2,5-dihydroxy-*p*-benzochinoate, benz (**3d**); 1,4-dihydroxy-anthrachinoate, anthra (**3e**)] were prepared either by reacting [AgNO₃] (**1**) with equimolar amounts of the corresponding β-diketones HL₂ [HL₂ = acetylacetonate, H-acac (**2a**); tropolone, H-trop (**2b**); 3-hydroxy-2-methyl-γ-pyranoate, H-pyro (**2c**)] (synthesis of the silver(I) salts **3a–3c**), or with the chinones H₂L₄ [H₂L₄ = 2,5-dihydroxy-*p*-benzochinone, H₂-benz (**2d**); 1,4-dihydroxy-anthraquinone, H₂-anthra (**2e**)] in a 2:1 molar ratio (synthesis of homobimetallic **3d** and **3e**) in presence of NEt₃ in ethanol solutions (Eqs. (1) and (2)). After appropriate work-up the silver(I) salts **3a–3e** can be isolated as light-sensitive solids in excellent yield (Table 1).

Complexes **3a–3e** are colourless (**3a**, **3b**), yellow (**3c**) or brown solids (**3d**, **3e**), which are poorly soluble in most common polar organic solvents, such as dimethylsulfoxide or dimethylformamide. Due to this low

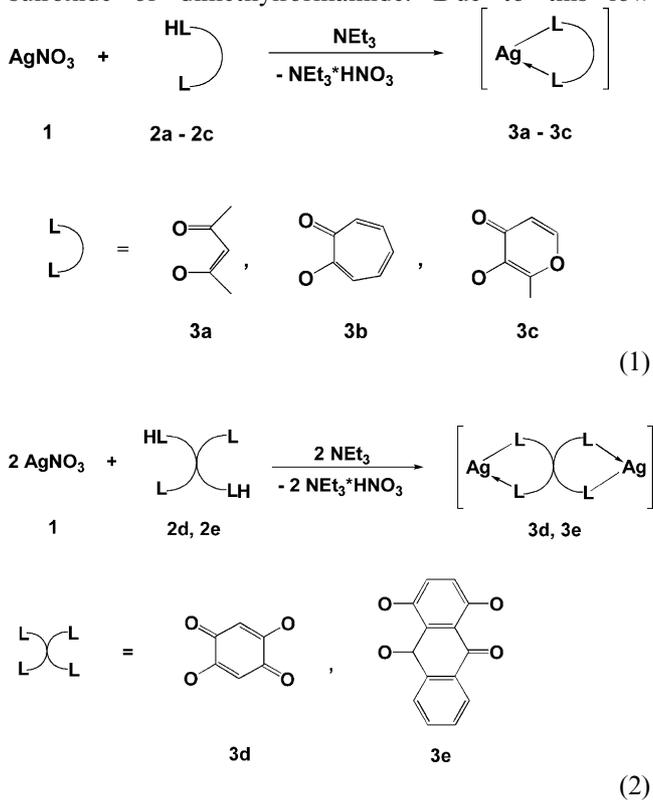


Table 1
Synthesis of the mono- and homobimetallic silver(I) salts **3a–3e**

Compound	L ₂ /L ₄	References
3a	acac ^a	[7,13]
3b	trop ^b	[9]
3c	pyro ^c	this work
3d	benz ^d	this work
3e	anthra ^e	this work

^a acac = acetylacetonate, C₅H₇O₂.

^b trop = tropolonate, C₇H₅O₂.

^c pyro = 3-hydroxy-2-methyl-γ-pyranoate, C₆H₅O₃.

^d benz = 2,5-dihydroxy-*p*-benzochinoate, C₆H₂O₄.

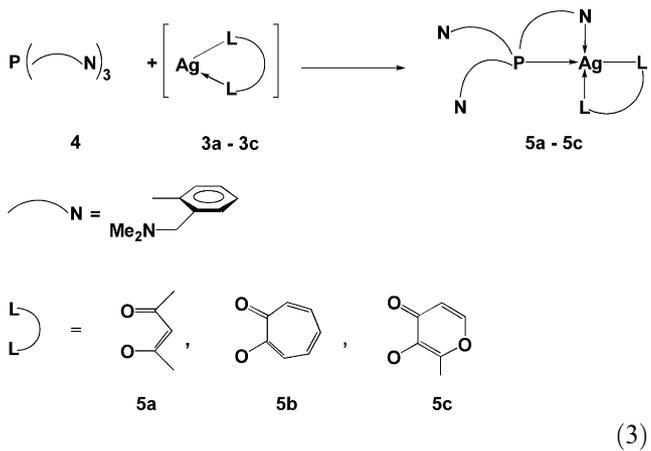
^e anthra = 1,4-dihydroxy-anthrachinoate, C₁₄H₆O₄.

solubility, which might favour multinuclear structures, complexes **3a–3e** could only be characterised by IR spectroscopy, elemental analysis and, for example, melting point determinations (Section 2).

As typical for β-diketonate complexes two characteristic frequencies are found in the vibrational spectra between 1500 and 1650 cm⁻¹ which can be assigned to the asymmetrical and symmetrical CO stretching frequencies [9,10]. The respective CO frequencies are separated by 40–90 cm⁻¹, indicating that in **3a–3e** symmetrical chelate-bound diketonates are present [9,10].

Since, **3b** is somewhat better soluble as the other species, additional ¹H and ¹³C{¹H} NMR spectroscopic studies could be carried out, which reveal to the proposed structure with a symmetrical chelate-bound trop ligand [11].

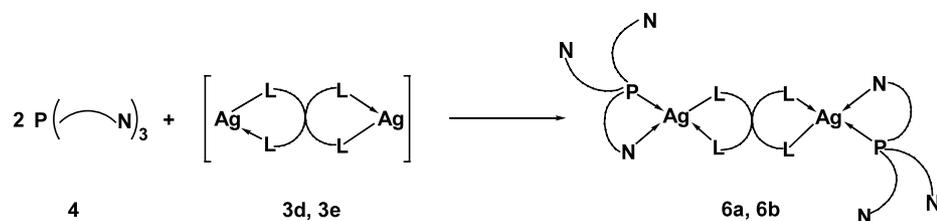
The silver salts **3a–3e** can successfully be used in the synthesis of mononuclear **5a–5c** and homobimetallic **6a** and **6b**. Treatment of equimolar amounts of **3a–3c** with P(C₆H₄CH₂NMe₂-2)₃ (**4**) in tetrahydrofuran at 25 °C produces the silver(I) complexes [P(C₆H₄CH₂NMe₂-2)₃]AgL₂ [L₂ = acetylacetonate (**5a**), tropolonate (**5b**), 3-hydroxy-2-methyl-γ-pyranoate (**5c**)] in very good yield (Eq. (3)). However, it is advisable to run the respective reactions in the dark since otherwise decomposition upon formation of colloidal silver takes place.



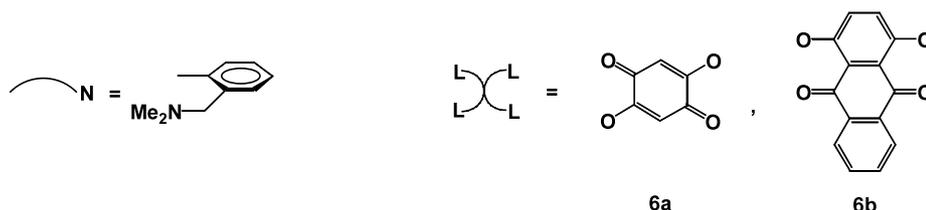
Homobimetallic silver(I) species of type $[P(C_6H_4CH_2NMe_2-2)_3]Ag-L_4-Ag[P(C_6H_4CH_2NMe_2-2)_3]$ [$L_4 = 2,5$ -dihydroxy-*p*-benzoquinone (**6a**), 1,4-dihydroxy-anthraquinone (**6b**)] in which the $[P(C_6H_4CH_2NMe_2-2)_3]Ag$ moieties are spanned by chinoate units are accessible, when **3d** or **3e**, respectively, are reacted with **4** in a 1:2 molar ratio in tetrahydrofuran under reflux for 3 h (Eq. (4)). Complexes **6a** and **6b** can be isolated in 93 or 94% yield.

colloidal silver. Therefore, it is advisable to store these species in the dark.

Carboxylates can act as mono- or bidentate or bridging ligands in transition metal chemistry [12]. Out of this reason we reacted $P(C_6H_4CH_2NMe_2-2)_3$ (**4**) with 1 equiv. of $[AgCO_2Me]$ (**7**) in tetrahydrofuran at 25 °C (Eq. (5)). After appropriate work-up, complex **8** could be obtained as a pale brown solid in 93% yield. When compared with **5** and **6** mononuclear **8** is very light-

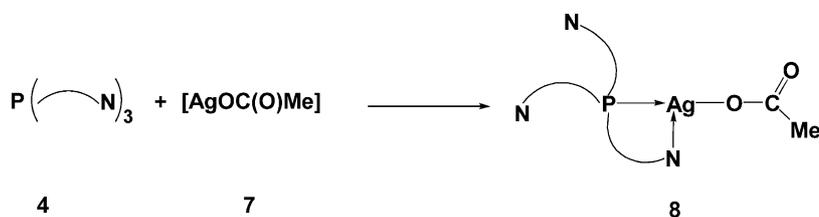


(4)

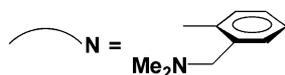


Complexes **5** and **6** are yellow (**5b**, **5c**), brown (**5a**) or red (**6a**, **6b**) solids, which are, when compared with **3a**–**3e**, much better soluble, e.g. in dichloromethane, diethyl

sensitive and, for example, rapidly decomposes in solution to afford a silver mirror on the Schlenk tube walls.



(5)



ether or tetrahydrofuran. While solid **5** and **6** are fairly stable to light, it appeared that solutions containing these species start to decompose on formation of

Nevertheless, from IR spectroscopic studies it is obvious that the acetate building block is only unidentate-bound to the silver atom, which clearly is

evidenced from the separation of the stretching vibrations of the CO units (see below), and could independently be confirmed by X-ray structure analysis of e.g. $[\text{P}(\text{C}_6\text{H}_4\text{CH}_2\text{NMe}_2)_3]\text{Ag}[\text{OC}(\text{O})\text{CF}_3]$ and $[\text{P}(\text{C}_6\text{H}_4\text{CH}_2\text{NMe}_2)_3]\text{Ag}[\text{OC}(\text{O})\text{CF}_2\text{CF}_3]$, respectively [13].

Complexes **5**, **6** and **8** were fully characterised by elemental analysis and spectroscopic studies (^1H , $^{13}\text{C}\{^1\text{H}\}$ and $^{31}\text{P}\{^1\text{H}\}$ NMR).

A noticeable feature in the IR spectra of these species is that two very distinct CO stretching vibrations (with exception of **6a**) appear between 1400 and 1650 cm^{-1} depending on the organic β -diketonate, chinoate or carboxylate building block present. While the separation for **5b** ($\Delta\nu = 76 \text{ cm}^{-1}$) points to a symmetrical-bound tropolonate unit, in **5c** and **6b** $\Delta\nu$ differs by 167 or 178 cm^{-1} , assembling asymmetric coordinated moieties [10,12].

The difference of the CO vibrations in **8** corresponds to a unidentate bonding situation of the carboxylic fragment to the Group-11 transition metal atom [12]. A similar behaviour was found in isostructural $[\text{P}(\text{C}_6\text{H}_4\text{CH}_2\text{NMe}_2)_3]\text{Ag}[\text{OC}(\text{O})\text{CF}_3]$ in which, as result from X-ray structure analysis, a distinct T-shaped arrangement for the P–Ag–O array is typical which probably arises from the constrained $\text{C}_6\text{H}_4\text{CH}_2\text{NMe}_2$ side arms [13a]. The same structural motif was found in $[\text{P}(\text{C}_6\text{H}_4\text{CH}_2\text{NMe}_2)_3]\text{Ag}[\text{OC}(\text{O})\text{CF}_2\text{CF}_3]$ [13b].

That in **5**, **6** and **8** the phosphane moiety $\text{P}(\text{C}_6\text{H}_4\text{CH}_2\text{NMe}_2)_3$ (**4**) is datively-bound to a silver(I) ion is nicely reflected by $^{31}\text{P}\{^1\text{H}\}$ NMR spectroscopy. For all complexes a distinguished resonance pattern of the phosphorus atom, due to its coupling to ^{107}Ag and ^{109}Ag isotopes is found. The respective resonance signals appear at approximately -27.0 (**5a**, **5b**, **8**) or at -29.5 ppm (**5c**, **6a**, **6b**) with 1J coupling constants of $^1J_{^{107}\text{Ag},^{31}\text{P}} = 550\text{--}640$ and $^1J_{^{109}\text{Ag},^{31}\text{P}} = 640\text{--}740$ Hz. Through the P→Ag bonding the ^{31}P resonance signals of **5**, **6** and **8** are shifted to lower field, when compared with the non-coordinated phosphane **4** (-37.2 ppm) [6]. This finding is in agreement with observations generally made by changing from free to datively-bound phosphanes in silver(I) chemistry [14].

The room temperature ^1H and $^{13}\text{C}\{^1\text{H}\}$ NMR spectra of **5**, **6** and **8** consists of resonance signals typical for the appropriate organic groupings present.

The NMR data of all new silver(I) complexes in solution imply fast dynamic rearrangements of the phosphane moiety. Thus, a single set of resonance signals for the three $\text{C}_6\text{H}_4\text{CH}_2\text{NMe}_2$ arms of the $\text{P}(\text{C}_6\text{H}_4\text{CH}_2\text{NMe}_2)_3$ entity is observed in the ^1H and $^{13}\text{C}\{^1\text{H}\}$ NMR spectra at 25 °C. This structural behaviour in solution was lately reported in detail, for example, for $[\text{P}(\text{C}_6\text{H}_4\text{CH}_2\text{NMe}_2)_3]\text{-copper(I)}$ and -silver(I) transition metal complexes [2,3].

Special features for **5**, **6** and **8** are the singlet for the six methyl groups, an AB pattern for the diastereotopic methylene protons and a pseudotriplett due to the aromatic proton in *ortho*-position to the phosphorus nucleus. The assignments have been supported by $^1\text{H}\{^{31}\text{P}\}$ NMR decoupling experiments.

The $^{13}\text{C}\{^1\text{H}\}$ NMR spectra of **5**, **6** and **8** in CDCl_3 are well defined and comprise sharp resonance signals. At 25 °C for the CH_3 and CH_2 units singlets are observed which is in agreement with the equivalence of the three built-in arms Me_2NCH_2 attributed to fast dynamic processes [2,3].

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