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Synthesis and structural characterization of silver(I) complexes with moon-shaped benzo[1,2-*b*;4,3-*b*']dithiophene phosphine derivative ligands

M. Helena Garcia^{a,*}, Pedro Florindo^a, M. Fátima M. Piedade^b, M. Teresa Duarte^b

^a Centro de Ciências Moleculares e Materiais, Faculdade de Ciências da Universidade de Lisboa, Ed.C8, Campo Grande, 1749-016 Lisboa, Portugal ^b Centro de Química Estrutural, Instituto Superior Técnico, Universidade Técnica de Lisboa, Av. Rovisco Pais, 1049-001 Lisboa, Portugal

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1. Introduction

The chemistry of poly-nuclear coordination complexes of coinage metals is a field of continuous growing due to the almost unlimited possibilities of chemical designs, ranging from simple molecules to polymeric arrangements [1,2]. Within this area, silver(I) complexes of the type $AgX/(PR_3)_n$, where X is a oxyanion such as NO₃⁻, ClO₄⁻, NO₂⁻ and CF₃SO₃⁻, are known to show interesting structural variations arising from different coordination modes of the anions [3-7]. Despite the intense investigation on the AgX/(PR₃)_n complexes, specially for R = Ph [3–7], complexes of the type $AgX/(PR_2R')_n$ were only sporadically investigated [6,8], nonetheless revealing that the identity of R' has a large influence both on silver(I) nuclearity and/or solid state packing features. Benzo[1,2-b;4,3-b']dithiophen-2-diphenylphosphine is an interesting ligand, in this respect, to study structural features induced by the large volume and moon-shape of the benzo[1,2*b*;4,3-*b*']dithiophene (bzt) group and also due to the possibility of this ligand to act as P,S-donor in a bridging bidentate fashion. In this paper we report the synthesis and spectroscopic characterization (¹H, ³¹P RMN) of novel silver(I) complexes of general formula $[Ag(O_3SCF_3)(PPh_2\{bzt\})_n]$ (*n* = 1–3), fully supported by single-crystal X-ray studies to understand the relationships between silver(I) nuclearity, CF₃SO₃⁻ coordinating ability and PPh₂{bzt} coordination modes. Also, comparison is made with related compounds to get some insight on the influence of the bzt group on silver nuclearity and solid state packing. Our results show that PPh₂{bzt} acts,

ABSTRACT

New silver complexes of general formula $[Ag(O_3SCF_3)(PPh_2\{bzt\})_n]$ (n = 1-3, bzt = benzo[1,2-b;4,3-b'] dithiophene) have been synthesized and characterized. Spectroscopic studies shown neutral ligand fluxionallity, typical of silver(1) complexes. The solid state structure of the complexes was determined by X-ray crystallographic studies, showing a decrease in structure complexity with increasing number of neutral ligands in silver coordination sphere: $[Ag(O_3SCF_3)(PPh_2\{bzt\})]$ is a dimer with two bridging triflate anions, further linked into polymeric bidimensional chains along *bc* plane, through Ag...Ph close contacts; $Ag(O_3SCF_3)(PPh_2\{bzt\})_2$] is also a dimmer with two bridging triflate anions, displaying an interesting packing feature, with *zig-zag* alignment of bzt groups along direction *b*; $[Ag(O_3SCF_3)(PPh_2\{bzt\})_3]$ is a monomer.

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in this case, only as P-donor and unravel beautiful and unexpected solid state packing features for these complexes.

2. Results and discussion

The ligand benzo[1,2-*b*;4,3-*b*']dithiophen-2-diphenylphosphine (**L1**) was synthesized based on the procedure reported for the synthesis of the analogue benzo[1,2-*b*;4,3-*b*']dithiophen-2-carbalde-hyde [9], by generation of the benzodithiophene α -anion with *n*-BuLi and subsequent treatment with (C₆H₅)₂PCl, affording **L1** in good yield (60%), as a colorless oil.

The silver complexes $[Ag(CF_3SO_3)(PPh_2\{bzt\})_n]$ (**nAg**: n = 1, 2 and 3) were prepared by reaction of $AgCF_3SO_3$ and an adequate molar ratio of **L1** (0.96, 2 and 3, respectively), in dichloromethane. The compounds were obtained as crystalline white solids, stable to air but slightly unstable to light in solution, soluble in dichloromethane, chloroform, acetone, acetonitrile and insoluble in tetrahydrofuran, ethyl ether and hydrocarbons.

The ¹H NMR spectra of the complexes only show the ligand resonances, slightly deshielded upon coordination to the metal center.

For compounds $[Ag(CF_3SO_3) (PPh_2 \{bzt\})]$ **1Ag**, $[Ag(CF_3SO_3)(PPh_2\{bzt\})_3]$ **3Ag** and for free **L1**, the resonances of proton H₃ are doublets, with coupling constants ranging from 6.8 to 11.2 Hz, attributed to P(-C-C-)H coupling, while it appears as a singlet in $[Ag(CF_3SO_3)(PPh_2\{bzt\})_2]$ **2Ag**.

Although the ³¹P NMR spectra of **L1** show a resonance at -17.06 as a sharp singlet, the complexes spectra obtained at room temperature revealed no resonances. This behavior is attributed to complexe's fluxionallity, due to the exchanging phenomena involving neutral ligands, typical of silver coordination chemistry [6]. At



^{*} Corresponding author. Tel.: +351 217500972; fax: +351 217500088. *E-mail address*: lena.garcia@fc.ul.pt (M.H. Garcia).

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-60 °C the spectra are resolved, showing the phosphorus resonances as two doblets, with Ag–P coupling constants ranging from 321.0 to 788.5 Hz, although for **1Ag** the second doublet isn't resolved. The large difference between Ag–P coupling constants is attributed both to the different s contribution to the hybridization of the silver centers [10] and to the different phosphorus/oxygen ratio in the silver coordination sphere [11].

2.1. Crystallographic studies

X-ray diffraction studies constitute an unambiguous way to determine both the nuclearity and the geometry of the silver compounds synthesized. In this case, infrared spectra are not useful to distinguish trifluoromethanesulfonate coordination modes, due to ambiguity in the attribution of CF_3 , SO_3 and **L1** vibrational modes [12].

Crystals of compounds **1Ag**, **2Ag** and **3Ag** were obtained by slow diffusion of *n*-hexane into dichloromethane solutions. Compound **1Ag** crystallizes in a centrosymmetric spatial group $(P_{2_1}/c, \text{monoclinic})$. This compound is a dinuclear derivative of $[Ag_2(CF_{3-}SO_3)_2(PPh_2\{bzt\})_2]$, in which two silver centers are bridged by two equivalent triflate anions using two donor oxygen atoms, O(1) and O(21), forming an eight-atom cycle (Fig. 1). Silver atoms deviate from planarity with the three coordinated atoms.

Table 1 presents selected bond lengths and angles for compound **1Ag**. The Ag(1)–P(1) distance is similar to the Ag-P distances determined for the analogous compounds $[Ag(CF_3SO_3)(PPh_3)]$ (2.3619(10)–2.3736(10)Å) and $[Ag(CF_3SO_3)(PPh_2Me)]$ (2.3628(11)–2.3637(10)Å) [6]; Ag–O distances are also in the interval verified for the referred compounds: 2.250(2)–2.572(3)Å and 2.2792(19)–2.573(2)Å, respectively.

Each silver atom of the dimer $[Ag_2(CF_3SO_3)_2(PPh_2\{bzt\})_2]$ establishes a short contact with a Ph carbon atom (C(125)) of a distinct dimer, the distance between the atoms being of 2.688(2) Å. This contact is not of the usual $Ag \cdots$ (aromatic bond) type, such as in the AgClO₄-benzene complex [13] since $Ag \cdots$ C contacts to C neighbor atoms are significantly longer. The Ag(1) \cdots C(125) contact is al-



Selected bond lengths and angles for compound 1Ag.

Bond lengths (Å)			
Ag1–O1 Ag1–O3#1 Ag1–P1	2.3045(17) 2.5028(17) 2.3738(6)	S1-01 S1-02 S1-03	1.4492(17) 1.425(2) 1.4354(17)
Ag1–C125#2	2.687(2)	51 05	1.1551(17)
Bond angles (°) O1-Ag1-O3#1 P1-Ag1-O3#1 O1-Ag1-P1 O3#1-Ag1-C125#2 P1-Ag1-C125#2	83.49(6) 110.82(4) 147.05(5) 77.28(7) 121.09(6)	O3–S1–O1 S1–O1–Ag1 S1–O3–Ag1#1 O1–Ag1–C125#2	113.83(11) 120.29(10) 147.81(11) 90.45(7)

Symmetry transformations used to generate equivalent atoms: #1: -x + 1, -y, -z;#2: x, -y + 1/2, z - 1/2.

most perpendicular to the Ph ring, with angles between this bond and other Ph carbon atoms ranging from 81.97° to 101.97° . A similar Ag. \cdot Ph close contact was found for compound [Ag(CF₃₋ SO₃)(PPh₂Me)] (2.721(3)) [6]. The arrangement of **L1** accounts for the establishment of the Ag(1) $\cdot \cdot \cdot$ C(125) short contact: the large bzt groups are almost perpendicular to the O(1)–Ag(1)–O(21) plane, minimizing the sterical hindrance on the silver center in the opposite side; also, a significant difference (approximately 36°) between angles O–Ag–P is verified, thus allowing the alignment of Ag(1) with C(125). Each dimeric unit interacts with four other units, leading to the formation of a bidimensional polymeric chain along the *bc* plane, packed along the *a* direction. This polymeric arrangement is illustrated in Fig. 2.

Compound **2Ag** is also a dinuclear derivative (Fig. 3) in which the molecule possesses an inversion center, with silver atoms displaying distorted tetrahedral coordination geometry. Each metal center is bonded to two phosphorus atoms of **L1** and two oxygen atoms of distinct, but crystallographically equivalent, triflate anions, forming an eight member cycle similar to the one found for **1Ag**. This structural arrangement is quite common in complexes of general formula [AgX(PPh₃)₂] [6,11]. Table 2 presents selected



Fig. 1. Molecular diagram of 1Ag with 50% thermal ellipsoids, showing the labeling scheme. Hydrogen atoms have been omitted for clarity.



Fig. 2. Perspective of the bidimensional polymeric chain of 1Ag along *a* (left) and *c* (right).



Fig. 3. Molecular diagram of 2Ag with 40% thermal ellipsoids, showing the labeling scheme. Hydrogen atoms have been omitted for clarity.

bond lengths and angles for compound **2Ag**. Both Ag–P (2.439(2) and 2.434(2) Å) and Ag–O distances are comparable to the ones found for compound $[Ag(O_3SCF_3)(PPh_3)_2]$ (2.409(5) and 2.572(5)) (Ag–P: 2.4321(12) and 2.4339(12); Ag–O: 2.385(13) to 2.578(5) [6]; Ag–O distances resemble the dissimilarity found in compound $[Ag(O_3SCF_3)(PPh_3)_2]$.

Worth noticing the effect of the substitution of one Ph ring by the larger bzt group: compounds $[Ag(O_3SCF_3)(PPh_3)]$ and

Table 2Selected bond lengths and angles for compound 2Ag.

Bond distances (Å)			
Ag1-01	2.572(5)	S1-01	1.442(5)
Ag1-03	2.411(5)	S1-O3#1	1.434(5)
Ag1–P1	2.439(2)	S1-02	1.414(5)
Ag1-P2	2.434(2)		
Bond angles (°)			
01-Ag1-03	84.32(15)	P1-Ag1-P2	126.35(7)
01-Ag1-P1	112.22(12)	S1-01-Ag1	127.1(3)
01-Ag1-P2	98.11(12)	S1#1-O3-Ag1	136.8(3)
O3-Ag1-P1	108.65(13)	03#1-S1-01	114.9(3)
O3-Ag1-P2	117.78(14)		

Symmetry transformations used to generate equivalent atoms: #1: -x + 1, -y, -z + 1.

 $[Ag(O_3SCF_3)(PPh_2\{bzt\})]$ (**1Ag**) have totally different solid state arrangements ($[Ag(O_3SCF_3)(PPh_3)]$ is a trinuclear derivative [6,14] while **1Ag** is a bidimensional polymer), compounds $[Ag(O_3SCF_3)(PPh_3)_2]$ and $[Ag(O_3SCF_3)(PPh_2\{bzt\})_2]$ (**2Ag**) have similar arrangements.

The four bzt groups of each dimer have an almost parallel alignment. This parallel alignment between bzt groups is maintained along direction *a*, through weak hydrogen bonding between the Ph groups and fluorine and oxygen atoms of neighbor dimers $(C(225)-H(225)\cdots F2 \{2.669(6) Å\}, (C(113)-H(113)\cdots O3 \{2.657(5) Å\}$ and $C(114)-H(114)\cdots F(1) \{2.635(6) Å\}$, forming a columnar packing. The column packing along the *b* direction is made, alternately, between columns symmetrically generated trough an 180° rotation around the *a* axis in relation to the neighbor ones, which results in a *zig-zag* alignment of the bzt groups along *b*, as illustrated in Fig. 4.

Compound **3Ag** · **0.5CH**₂**Cl**₂ crystallizes in the triclinic centrosymmetric space group $P\bar{1}$. The asymmetric unit (Fig. 5) is the monomeric formula unit with the half solvent molecule of CH₂Cl₂. Selected bond lengths and angles are presented in Table 3.

The silver atom is coordinated to three phosphorus atoms of **L1** ligands and to an oxygen atom (O1) of trifluoromethanesulfonate, displaying a distorted tetrahedral coordination. The Ag–P bond distances range from 2.4780(12) to 2.5113(11) Å and are shorter



Fig. 4. Perspective of the supramolecular arrangement of **2Ag**, along direction *c*: dimer alignment along direction *a* (horizontal) and *zig-zag* alignment of bzt groups along *b* (vertical).

than the ones found for compounds $[AgX(PPh_3)_3]$ (X = Cl: 2.558(5)–2.582(4); Br: 2.528(3)–2.549(7); I: 2.544(2)–2.780(3) [15]; NO₃: 2.525(1)–2.630(2) [11]; CO₂C₂F₅: 2.5432(7)–2.6026(8) Å [16]). P–Ag–P angles range between 111.49(4) and 124.67(4) Å: the angle



Fig. 5. Molecular diagram of **3Ag** with 40% thermal ellipsoids, showing the labeling scheme. Hydrogen atoms have been omitted for clarity.

Table 3

Selected bond lengths and angles for compound $\textbf{3Ag} \cdot \textbf{0.5CH}_2\textbf{Cl}_2.$

Bond lengths (Å)			
Ag1-01	2.527(5)	S1-01	1.414(4)
Ag1–P1	2.4886(12)	S1-02	1.417(4)
Ag1–P2	2.5113(11)	S1-03	1.445(5)
Ag1-P3	2.4780(12)		
Bond angles (°)			
P1-Ag1-P2	111.49(4)	01-Ag1-P3	105.75(12)
P1-Ag1-P3	124.67(4)	S1-01-Ag1	151.0(3)
P2-Ag1-P3	112.28(4)	01-S1-02	119.0(3)
O1-Ag1-P1	100.70(13)	01-S1-03	112.1(3)
01-Ag1-P2	97.04(11)	02-S1-03	113.1(3)

P(1)-Ag(1)-P(3) is higher (~23 Å) than the other two P-Ag-P angles, minimizing the interaction between **L1** ligands and the anion, and opposite to the longer Ag-P(2) distance, as expected.

3. Experimental

3.1. General procedures

All the experiments were carried out under a dinitrogen atmosphere, using standard Schlenk techniques. All solvents used were dried using standard methods [17]. AgCF₃SO₃ and $(C_6H_5)_2$ PCl were purchased from Aldrich and used without further purification. ¹H and ³¹P NMR spectra were recorded on a Bruker Avance 400 spectrometer at probe temperature, unless stated otherwise. The ¹H NMR (chloroform-*d*) chemical shifts are reported in parts per million (ppm) downfield from internal Me₄Si and the ³¹P NMR (chloroform-*d*) spectra are reported in ppm downfield from external standard, 85% H₃PO₄. Elemental analyses were obtained at *Laboratório de Análises, Instituto Superior Técnico*, using a Fisons

Table 4	
Details of data collection and structure refinement for complexes 1Ag . 2Ag and 3Ag .	

Compound	1Ag	2Ag	$3Ag \cdot 0.5CH_2Cl_2$
Chemical formula	$C_{23}H_{15}AgF_{3}O_{3}PS_{3}$	$C_{45}H_{30}AgF_{3}O_{3}P_{2}S_{5}$	C _{67.5} H ₄₅ AgClF ₃ O ₃ P ₃ S ₇
Formula weight	631.37	1005.80	1421.68
T (K)	150(2)	150(2)	150(2)
Wavelength	0.71073	0.71073	0.71073
Crystal system	monoclinic	monoclinic	triclinic
Space group	P2 ₁ /c	$P2_1/n$	ΡĪ
a (Å)	11.2634(9)	12.631(4)	11.2932(7)
b (Å)	18.7654(13)	22.428(7)	12.2422(8)
c (Å)	11.4873(8)	15.754(5)	24.8700(16)
α(°)	90	90	80.429(4)
β (°)	100.619(4)	103.18(2)	86.819(4)
γ (°)	90	90	65.425(4)
$V(Å^3)$	2386.4(3)	4346(2)	3083.0(3)
Ζ	4	4	2
Ζ'	0.5	0.5	1
D_{calc} (g cm ⁻³)	1.757	1.537	1.531
Absorption coefficient (mm ⁻¹)	1.222	0.831	0.743
F(000)	1256	2032	1444
θ Range for data collection (°)	2.82-26.37	1.87-27.70	1.91-27.60
Limiting indices	$-14 \leq h \leq 14, -23 \leq k \leq 23, -14 \leq l \leq 14$	$-15 \leq h \leq 16, -28 \leq k \leq 28, -20 \leq l \leq 20$	$-14 \leq h \leq 14, -15 \leq k \leq 15, -32 \leq l \leq 29$
Reflections collected/unique (R _{int})	70062/4864 (0.0531)	44956/10055 (0.1594)	42714/13939 (0.0693)
Completeness to theta	26.37 (99.8%)	27.70 (98.5%)	27.60 (97.5%)
Refinement method	full-matrix least-squares on F ²	full-matrix least-squares on F ²	full-matrix least-squares on F^2
Data/restraints/parameters	4864/0/307	10055/0/532	13939/0/768
Goodness-of-fit on F^2	1.024	0.994	1.026
Final <i>R</i> indices $[I > 2\sigma(I)]$	$R_1 = 0.0267, wR_2 = 0.0592$	$R_1 = 0.0689, wR_2 = 0.1612$	$R_1 = 0.0575, wR_2 = 0.1295$
Largest difference in peak/hole ($e Å^{-3}$)	0.838/-0.441	0.750/-1.107	1.746/-0.990

Instruments EA1108 system. Data acquisition, integration and handling were performed using a PC with software package EA-GER-200 (Carlo Erba Instruments).

3.2. Synthesis of benzo[1,2-b;4,3-b']dithiophen-2-diphenylphosphine (L1)

To a THF solution (15 mL) of benzo[1,2-b;4,3-b']dithiophene (0.19 g, 1 mmol) cooled at -78 °C, was slowly added a 2.0 M *n*-BuLi pentane solution (0.55 mL, 1.1 mmol). The mixture was stirred at -78 °C for 5 min and for 15 min at room temperature. The resulting yellow solution was cooled at -78 °C and treated with Ph₂PCl (0.22 mL, 1.2 mmol). After 1 h under agitation at -78 °C, the solution was warmed to room temperature and quenched with a saturated solution of NH₄Cl (5 mL). The THF was removed under reduced pressure, the crude material was taken up with CH₂Cl₂ (20 mL) and washed with saturated aqueous solution of NH₄Cl $(3 \times 10 \text{ mL})$ and water $(3 \times 10 \text{ mL})$. The organic phase was dried over MgSO₄, the solvent was removed under reduced pressure and the crude material was purified by means of flash column chromatography (eluent: light petroleum/CH₂Cl₂ 4:1). Yield: 60%. Colorless oil. Anal. (%): Calc. for C22H15PS2: C, 70.56; H, 4.04; S, 17.13. Found: C, 70.01; H, 3.95; S, 17.35. ¹H NMR: 7.30 (m, 6H, Ph), 7.38 (m, 4H, Ph), 7.47 (d, 1H, H_{10} , J_{HH} = 5.2 Hz), 7.59 (d, 1H, H_{11} , J_{HH} = 5.2 Hz), 7.62 (d, 1H, H_7 , J_{HH} = 8.4 Hz), 7.71 (d, 1H, H_6 , $J_{\rm HH}$ = 8.4 Hz), 8.02 (d, 1H, H₁₀, $J_{\rm HP}$ = 6.8 Hz). ³¹P NMR: -17.06 (s).

3.3. Synthesis of the complexes $[Ag(CF_3SO_3)(PPh_2\{bzt\})_n]$

Complexes of general formula $[Ag(CF_3SO_3)(PPh_2\{bzt\})_n]$ were prepared from AgCF_3SO_3 (0.128 g, 0.5 mmol) in CH_2Cl₂, in the presence of an adequate quantity of benzo[1,2-*b*;4,3-*b'*]dithiophen-2diphenylphosphine (*n* = 1: 0.180 g, 0.49 mmol; *n* = 2: 0.374 g, 1.00 mmol; *n* = 3: 0.562 g, 1.5 mmol). The mixtures were stirred overnight at room temperature, protected from light. After filtering and reducing the solvent volume to \approx 5 mL), the complexes were recrystallized by slow diffusion of n-hexane, affording white crystalline products.

3.3.1. [Ag(CF₃SO₃)(PPh₂{bzt})] (1Ag)

Yield: 94%. White. *Anal.* (%): Calc. for $C_{23}H_{15}S_3O_3PF_3Ag$: C, 43.75; H, 2.39; S, 15.24. Found: C, 44.12; H, 2.39; S, 15.92. ¹H NMR: 7.50 (m, 6H, PPh₂), 7.59 (m, 4H, PPh₂), 7.61 (d, 1H, H₁₀, *J*_{HH} = 4.8 Hz), 7.70 (d, 1H, H₇, *J*_{HH} = 8.8 Hz), 7.76 (d, 1H, H₁₁, *J*_{HH} = 5.2 Hz), 7.88 (d, 1H, H₆, *J*_{HH} = 8.4 Hz), 8.39 (d, 1H, H₃, *J*_{HP} = 11.2 Hz). ³¹P NMR (-60 °C): 3.23 (d, *J*(¹⁰⁹Ag–P) = 788.5 Hz).

3.3.2. $[Ag(CF_3SO_3)(PPh_2\{bzt\})_2]$ (**2Ag**)

Yield: 89%. White. *Anal.* (%): Calc. for $C_{45}H_{30}S_5O_3P_2F_3A_5 \\ 0.3CH_2CI_2: C, 52.76; H, 2.99; S, 15.54. Found: C, 52.84; H, 3.11; S, 15.60. ¹H NMR: 7.38 (m, 4H, PPh_2), 7.48 (m, 2H, PPh_2), 7.53 (d, 1H, H_{10}, J_{HH} = 5.2 Hz), 7.59 (m, 4H, PPh_2), 7.63 (d, 1H, H_{11}, J_{HH} = 4.8 Hz), 7.64 (d, 1H, H_6, J_{HH} = 8.8 Hz), 7.85 (d, 1H, H_6, J_{HH} = 8.8 Hz), 8.46 (s, 1H, H_3). ³¹P NMR (-60 °C): 0.79 (dd, J(¹⁰⁹Ag-P) = 553.3, 488.4 Hz).$

3.3.3. $[Ag(CF_3SO_3)(PPh_2\{bzt\})_3]$ (**3**Ag)

Yield: 82%. White. *Anal.* (%): Calc. for $C_{67}H_{45}S_7O_3P_3F_3Ag \cdot 0.4CH_2Cl_2$: C, 57.24; H, 3.26; S, 15.87. Found: C, 57.12; H, 3.32; S, 15.88. ¹H NMR: 7.08 (m, 4H, PPh₂), 7.23 (m, 2H, PPh₂), 7.38 (d, 1H, H₁₀, *J*_{HH} = 5.6 Hz), 7.40 (d, 1H, H₁₁, *J*_{HH} = 5.6 Hz), 7.42 (m, 4H, PPh₂), 7.51 (d, 1H, H₆, *J*_{HH} = 8.8 Hz), 7.75 (d, 1H, H₆, *J*_{HH} = 8.8 Hz), 8.34 (d, 1H, H₃, *J*_{HP} = 7.2 Hz). ³¹P NMR (-60 °C): 2.90 (dd, *J*(¹⁰⁹Ag-P, ¹⁰⁷Ag-P) = 362.5, 321.0 Hz).

3.4. Crystal structure determination

X-ray data for compounds **1Ag**, **2Ag** and **3Ag** · **0.5CH₂Cl₂** were collected on a Bruker AXS APEX CCD area detector diffractometer at 150(2) K using graphite-monochromated Mo K α (λ = 0.71073 Å) radiation. Intensity data were corrected for Lorentz polarization effects. Empirical absorption correction using sADABS [18] was applied and the data reduction was done with SMART and SAINT programs [19].

All structures were solved by direct methods with sirg97 [20] and sir2004 [21] and refined by full-matrix least-squares on F^2 with shelxl97 [22], all included in the package of programs wingx-Version

1.70.01 [23]. Non-hydrogen atoms were refined with anisotropic thermal parameters whereas H-atoms were placed in idealized positions and allowed to refine riding on the parent C atom. Graphical representations were prepared using ORTEP [24], and MERCURY 1.1.2 [25]. A summary of the crystal data, structure solution and refinement parameters are given in Table 4. In compound **2Ag** a severely disordered solvent molecule was found that could not be modeled so it was removed using SQUEEZE [26]. SQUEEZE calculated an electron count/cell of 143 which matches well with a n-hexane or a dichloromethane molecule per asymmetric unit. Before SQUEEZE $R_1 = 0.0801$, afterwards $R_1 = 0.0764$.

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Appendix A. Supplementary data

CCDC 122345 and 123454 contain the supplementary crystallographic data for **1Ag** and **3Ag**. These data can be obtained free of charge via http://www.ccdc.cam.ac.uk/conts/retrieving.html, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or e-mail: deposit@ccdc.cam.ac.uk. Supplementary data associated with this article can be found, in the online version, at doi:10.1016/ j.poly.2008.11.013.

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