Inorganic Chemistry Communications 15 (2012) 117–120

Contents lists available at SciVerse ScienceDirect

Inorganic Chemistry Communications

journal homepage: www.elsevier.com/locate/inoche

Decomposition of the mixed-ligand silver(I) complex $[Ag(PPh_3)_2\{Et_2NC(S)NP(S)(OiPr)_2\}]$ with the formation of $[Ag(PPh_3)\{Et_2NC(S)NP(S)(OiPr)_2\}]$, $[Ag(PPh_3)_3NCS]\cdot(CH_3)_2C{=}O$ and $Et_2NP(S)(OiPr)_2$

Maria G. Babashkina [a,*], Damir A. Safin [a], Michael Bolte [b], Yann Garcia [a]

[a] *Institute of Condensed Matter and Nanosciences, MOST - Inorganic Chemistry, Université Catholique de Louvain, Place L. Pasteur 1, 1348 Louvain-la-Neuve, Belgium*
[b] *Institut für Anorganische Chemie J.-W.-Goethe-Universität, Frankfurt/Main, Germany*

ARTICLE INFO

Article history:
Received 21 August 2011
Accepted 5 October 2011
Available online 12 October 2011

Keywords:
Coordination chemistry
Crystal structure
Decomposition
N-thiophosphoryl thiourea
Silver(I)

ABSTRACT

Reaction of the potassium salt of the *N*-thiophosphorylated thiourea $Et_2NC(S)NHP(S)(OiPr)_2$ (**HL**) with a mixture of $AgNO_3$ and PPh_3 in aqueous $EtOH/CH_2Cl_2$ leads to the mixed-ligand silver(I) complex $[Ag(PPh_3)_2\{Et_2NC(S)NP(S)(OiPr)_2\}]$ (**[Ag(PPh$_3$)$_2$L]**). Recrystallization of **[Ag(PPh$_3$)$_2$L]** from an acetone/*n*-hexane mixture leads to the decomposition of the starting complex with the formation of $[Ag(PPh_3)\{Et_2NC(S)NP(S)(OiPr)_2\}]$ (**[Ag(PPh$_3$)L]**), **[Ag(PPh$_3$)$_3$NCS]·(CH$_3$)$_2$C=O** and **Et$_2$NP(S)(O*i*Pr)$_2$**. The structures of **[Ag(PPh$_3$)$_2$L]**, **[Ag(PPh$_3$)L]**, **[Ag(PPh$_3$)$_3$NCS]·(CH$_3$)$_2$C=O** and **Et$_2$NP(S)(O*i*Pr)$_2$** were all investigated by IR, $^{31}P\{^1H\}$ and ^1H NMR spectroscopy, and their compositions were established by elemental analysis. The crystal structure of the complex **[Ag(PPh$_3$)$_3$NCS]·(CH$_3$)$_2$C=O** obtained from single crystal X-ray diffraction is presented.

Recently, we have described mixed-ligand Cu(I) complexes with a number of *N*-thiophosphorylated thioureas and thioamides $RC(S)NHP(S)(OiPr)_2$ (**NTT**) ($R = NH_2$, MeNH, *i*PrNH, *t*BuNH, PhNH, 2,6-$Me_2C_6H_3NH$, 2,4,6-$Me_3C_6H_2NH$, $(EtO)_2P(O)CH_2C_6H_4$-4-NH, α-naphthyl-NH, pyridin-2-yl-NH, pyridin-3-yl-NH, H_2N-6-Py-2-NH, Me_2N, Et_2N, morpholin-*N*-yl, piperidin-*N*-yl, Ph) [1–12] or *N*-thiophosphorylated bis-thioureas $Z\{NHC(S)NHP(S)(OiPr)_2\}_2$ ($Z = o$-C_6H_4, 1,2-CH_2CH_2) [11,12], and triphenylphosphane or $Ph_2P(CH_2)_{1-3}PPh_2$ and $Ph_2P(C_5H_4FeC_5H_4)PPh_2$ phosphanes. The reaction of alkaline salts of the tetrakis-thiourea, containing a cyclam fragment, with $[Cu(PPh_3)_3I]$ leads to the tetranuclear Cu(I) complex $[\{Cu(PPh_3)_2\}_4(cyclam)]$ [13]. However, there are only three publications on mixed-ligand Ag(I) complexes with **NTT** (R = PhNH, α-naphthyl-NH, pyridin-3-yl-NH, $C_5H_{10}N$, Ph) [14–16]. It was established that depending on the synthesis conditions one or two molecules of PPh_3 are coordinated to the metal center. Furthermore, some of the described Ag(I) complexes show luminescent properties in the solid state [15] and are excellent precursors for the silver nanoparticles [16].

In this contribution, we report on the synthesis and characterization of the mixed-ligand silver(I) complex $[Ag(PPh_3)_2\{Et_2NC(S)NP(S)(OiPr)_2\}]$ (**[Ag(PPh$_3$)$_2$L]**) with $Et_2NC(S)NHP(S)(OiPr)_2$ (**HL**) and triphenylphosphane. The decomposition of the complex **[Ag(PPh$_3$)$_2$L]** in an acetone/*n*-hexane mixture is also studied.

The *N*-thiophosphorylated thiourea **HL** was synthesized as previously described by the treatment of Et_2NH with the isothiocyanate $(iPrO)_2P(S)NCS$ [1,2]. The complex **[Ag(PPh$_3$)$_2$L]** was prepared by the following procedure: the ligand was deprotonated *in situ* using KOH, followed by reaction with a mixture of $AgNO_3$ and PPh_3 (Scheme 1) [17]. The complex was obtained as a colorless crystalline solid, which is soluble in most polar solvents.

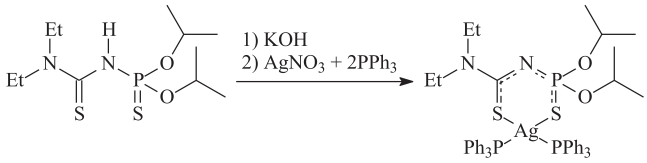
It is noteworthy that recrystallization of the complex **[Ag(PPh$_3$)$_2$L]** from an acetone/*n*-hexane mixture leads to the decomposition of the starting complex with the formation of $[Ag(PPh_3)\{Et_2NC(S)NP(S)(OiPr)_2\}]$ (**[Ag(PPh$_3$)L]**), **[Ag(PPh$_3$)$_3$NCS]·(CH$_3$)$_2$C=O** and **Et$_2$NP(S)(O*i*Pr)$_2$**[17]. Nothing similar was observed using other solvents. In all cases we were able to isolate fine crystalline **[Ag(PPh$_3$)$_2$L]**. Unfortunately, we were not able to obtain X-ray suitable crystals of **[Ag(PPh$_3$)$_2$L]** using other solvents. It should be noted, that no similar reactions were observed for the recently reported mixed-ligand Ag(I) complexes with **NTT** and phosphanes [14–16], even for the complex with the piperidine substituent at the thiocarbonyl fragment [16], which is a close analogue of the complex **[Ag(PPh$_3$)$_2$L]**.

Recently, we have established that the reaction of $AgNO_3$ with the potassium salt of the *N*-thiophosphorylated thiourea $NH_2C(S)NHP(S)(OiPr)_2$ gave a new supramolecular silver(I) complex, $[Ag(N{\equiv}C{-}NP(S)(OiPr)_2)]_n$, which contains both tri- and tetracoordinated Ag(I) [18]. The starting ligand had undergone a rearrangement forming the corresponding cyanamido ligand, while the sulfur has been stripped from the starting thiourea forming H_2S and/or K_2S. Furthermore, Othman et al.

---

* Corresponding author.
E-mail address: maria.babashkina@ksu.ru (M.G. Babashkina).

1387-7003/$ – see front matter © 2011 Elsevier B.V. All rights reserved.
doi:10.1016/j.inoche.2011.10.005



Scheme 1. Preparation of the complex **[Ag(PPh$_3$)$_2$L]**.

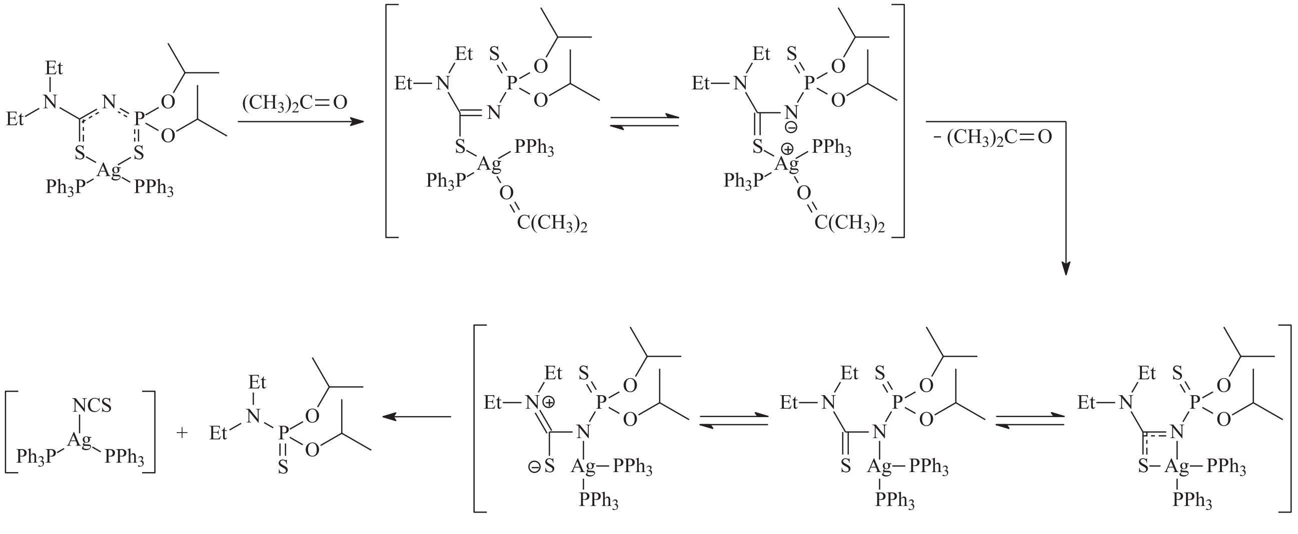
have described the formation of the complex **[Ag(PPh$_3$)$_3$NCS]·CHCl$_3$** by the treatment of the dimeric silver(I) complex [Ag$_2$(PPh$_3$)$_2$(CH$_3$COO)$_2$] with thiosemicarbazide in the ethanol/chloroform mixture [19]. We suggest, that the acetone molecule provokes the decomposition of **[Ag(PPh$_3$)$_2$L]** through the coordination to Ag(I) with the subsequent opening of a six-membered chelate ring, which, in turn, is unstable due to the influence of the strong electron donor NEt$_2$ group (Scheme 2). This leads to a rearrangement of the anionic ligand with the elimination of the NCS group. Thus, the compound **Et$_2$NP(S)(O*i*Pr)$_2$** is formed. The tricoordinated complex **[Ag(PPh$_3$)$_2$NCS]** reacts with another molecule of **[Ag(PPh$_3$)$_2$L]** with the formation of **[Ag(PPh$_3$)L]** and **[Ag(PPh$_3$)$_3$NCS]** (Scheme 3). Recently, we have reported the similar tricoordinated Cu(I) complexes [Cu(PPh$_3$)RC(S)NP(S)(O*i*Pr)$_2$] (R=NH$_2$, (EtO)$_2$P(O)CH$_2$C$_6$H$_4$-4-NH) [4,11,12].

The structures of **[Ag(PPh$_3$)$_2$L]**, **[Ag(PPh$_3$)L]**, **[Ag(PPh$_3$)$_3$NCS]·(CH$_3$)$_2$C=O** and **Et$_2$NP(S)(O*i*Pr)$_2$** were investigated by IR, ^{31}P{^{1}H} and ^{1}H NMR spectroscopy, their compositions were established by elemental analysis. The crystal structure of **[Ag(PPh$_3$)$_3$NCS]·(CH$_3$)$_2$C=O** was established from single crystal X-ray diffraction.

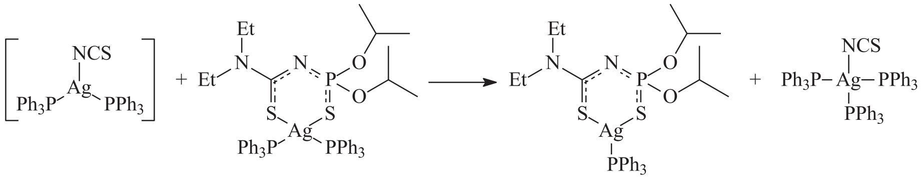
The IR spectra of the complexes **[Ag(PPh$_3$)$_2$L]** and **[Ag(PPh$_3$)L]** contain a band at 600 and 596 cm^{-1}, respectively, for the P=S group of the anionic ligand. These bands are shifted to low frequencies relative to the parent ligand [1,2] as a result of coordination to the Ag(I) ion. The same band in the IR spectrum of **Et$_2$NP(S)(O*i*Pr)$_2$** was observed at 611 cm^{-1}, which is in the region that is characteristic for similar thiophosphorylamides R^{1}R^{2}P(S)(OR^3)$_2$ [20]. In the spectra of **[Ag(PPh$_3$)$_2$L]** and **[Ag(PPh$_3$)L]** there is a band at 1479 and 1521 cm^{-1}, respectively, corresponding to the conjugated SCN fragment. In addition, there is a broad intense band arising from the POC group at 970–984 cm^{-1} in the spectra of **[Ag(PPh$_3$)$_2$L]**, **[Ag(PPh$_3$)L]** and **Et$_2$NP(S)(O*i*Pr)$_2$**. The IR spectrum of the complex **[Ag(PPh$_3$)$_3$NCS]·(CH$_3$)$_2$C=O** contains the characteristic bands for the C=S and C=N groups at 793 and 1997 cm^{-1}, respectively. These bands are in the corresponding regions that are characteristic for the terminal thiocyanate group bonded through the nitrogen atom to the metal center [21,22]. The acetone molecule in the IR spectrum of the acetone solvate is shown as a band at 1701 cm^{-1}, corresponding to the C=O group.

In the ^{31}P{^{1}H} NMR spectra of the complexes **[Ag(PPh$_3$)$_2$L]** and **[Ag(PPh$_3$)L]** the resonances at 51.1 and 51.4 ppm, respectively, correspond to the phosphorus atom of the thiophosphoryl group. These signals are shifted high-field relative to that in the spectrum of **HL** [1,2]. The signals of the phosphorus atoms of PPh$_3$ in the spectra of the complexes **[Ag(PPh$_3$)$_2$L]**, **[Ag(PPh$_3$)L]** and **[Ag(PPh$_3$)$_3$NCS]·(CH$_3$)$_2$C=O** are found at 5.0, 4.7 and 4.8 ppm, respectively. These signals are markedly low-field shifted compared to that in the spectrum of the relative Cu(I) complex **[Cu(PPh$_3$)$_2$L]** with the same ligand **HL** [1,2]. The signal of the phosphorus atom in the ^{31}P{^{1}H} NMR spectrum of **Et$_2$NP(S)(O*i*Pr)$_2$** was observed at 4.8 ppm, which is in the region that is characteristic for similar thiophosphorylamides R^{1}R^{2}P(S)(OR^3)$_2$ [20,23].

The ^{1}H NMR spectra of **[Ag(PPh$_3$)$_2$L]**, **[Ag(PPh$_3$)L]** and **Et$_2$NP(S)(O*i*Pr)$_2$** contain a set of signals for the *i*Pr and Et protons: signals for the CH$_3$ protons at 1.13–1.34 ppm and signals for the CH$_2$ and CH protons at 3.58–3.92 and 4.53–4.89 ppm, respectively. Signals of the Et groups in the spectra of the complexes **[Ag(PPh$_3$)$_2$L]** and **[Ag(PPh$_3$)L]** are doubled due to hindered rotation, while the methyl protons of the isopropyl groups are diastereotopic and show two signals. The signals for the phenyl protons in the spectra of the complexes **[Ag(PPh$_3$)$_2$L]**, **[Ag(PPh$_3$)L]** and **[Ag(PPh$_3$)$_3$NCS]·(CH$_3$)$_2$C=O** are observed as a multiplet at 7.08–7.50 ppm. The signal for the acetone



Scheme 2. Decomposition of the complex **[Ag(PPh$_3$)$_2$L]** in the acetone solution.



Scheme 3. Formation of the complexes **[Ag(PPh$_3$)L]** and **[Ag(PPh$_3$)$_3$NCS]**.

Table 1
Crystal data and data collection details for **[Ag(PPh$_3$)$_3$NCS]·(CH$_3$)$_2$C=O** and **[Ag(PPh$_3$)$_3$NCS]·CHCl$_3$**[19].

	[Ag(PPh$_3$)$_3$NCS]·(CH$_3$)$_2$C=O	[Ag(PPh$_3$)$_3$NCS]·CHCl$_3$ [19]
Empirical formula	$C_{58}H_{51}AgNOP_3S$	$C_{56}H_{46}AgCl_3NP_3S$
Formula weight	1020.84	1072.13
Crystal system	Triclinic	Triclinic
Space group	*P 1*	*P 1*
a (Å)	13.1427(5)	13.329(2)
b (Å)	13.6233(5)	13.647(1)
c (Å)	14.2212(5)	14.467(1)
α (°)	89.598(2)	89.70(1)
β (°)	79.058(2)	79.47(1)
γ (°)	80.483(2)	80.09(1)
V (Å^3)	2464.78(16)	2547.7(5)
Z	2	2
D_{calc} (g cm^{-3})	1.362	1.398
T (*K*)	173(2)	293(2)
μ (mm^{-1})	0.590	0.726
Reflections collected	64,157	13,101
Unique reflections	8678	8877
Observed reflections	17,834 ($R_{int}=0.0178$)	11,600 ($R_{int}=0.0165$)
Final *R* indices [$I>2\sigma(I)$]	$R_1=0.0334$, $wR_2=0.0892$	$R_1=0.0513$, $wR_2=0.1641$

CH$_3$ protons is observed at 2.10 ppm in the ^{1}H NMR spectrum of **[Ag(PPh$_3$)$_3$NCS]·(CH$_3$)$_2$C=O**.

The crystal structure of the solvate **[Ag(PPh$_3$)$_3$NCS]·(CH$_3$)$_2$C=O** was determined by a single crystal X-ray diffraction analysis (Table 1) [24]. The molecular structure of the acetone solvate complex in the crystal is shown in Fig. 1. Selected bond lengths and bond angles are given in Table 2. The crystal structure of another solvate (with chloroform) was earlier described [19]. The cell parameters, bond lengths, and bond and torsion angles of ref. [19] are similar to our structure (Tables 1 and 2), the differences observed being due to the lower temperature (173 K) of our measurement compared to the previous report (293 K).

The crystal structure of **[Ag(PPh$_3$)$_3$NCS]·(CH$_3$)$_2$C=O** was solved and refined in the triclinic space group *P 1*. In the structure of the acetone solvate, the Ag(I) cation is in a NP$_3$ tetrahedral environment formed by three phosphorus atoms of the triphenylphosphane ligands and the nitrogen atom of the isothiocyanate ligand (Fig. 1). The angles about the silver atom deviate significantly from 100.72(4)° to 114.821(13)°. The N(1)–C(1)–S(1) angle is 179.8(2)° indicating the linearity of this fragment. The Ag(1)–N(1)–C(1) angle is 160.14(15)° and fits well in the range characteristic for the majority of the M–NCS complexes [19].

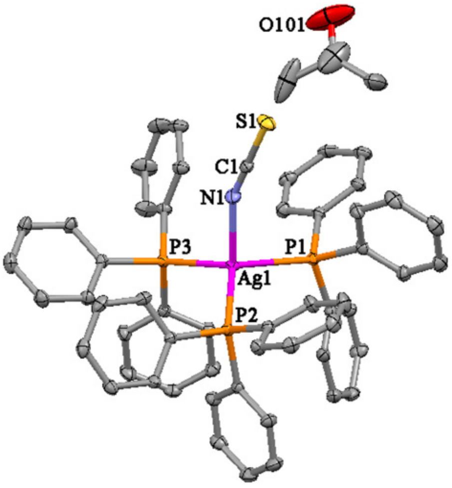


Fig. 1. Molecular structure of the complex **[Ag(PPh$_3$)$_3$NCS]·(CH$_3$)$_2$C=O**. Thermal ellipsoids are drawn at the 30% probability level, hydrogen atoms were omitted for clarity.

Table 2
Selected bond lengths (Å), and bond angles (°) for [Ag(PPh$_3$)$_3$NCS]·(CH$_3$)$_2$ C=O and [Ag(PPh$_3$)$_3$NCS]·CHCl$_3$[19].

	[Ag(PPh$_3$)$_3$NCS]·(CH$_3$)$_2$ C=O	[Ag(PPh$_3$)$_3$NCS]·CHCl$_3$ [19]
Bond lengths		
Ag(1)–N(1)	2.3111(16)	2.319(4)
Ag(1)–P(1)	2.5825(4)	2.5967(9)
Ag(1)–P(2)	2.5208(4)	2.5431(9)
Ag(1)–P(3)	2.5353(4)	2.5561(9)
N(1)–C(1)	1.150(2)	1.145(5)
C(1)–S(1)	1.6361(18)	1.635(4)
Bond angles		
Ag(1)–N(1)–C(1)	160.14(15)	159.6(3)
N(1)–C(1)–S(1)	179.8(2)	178.8(4)
N(1)–Ag(1)–P(1)	100.72(4)	102.58(10)
N(1)–Ag(1)–P(2)	105.15(5)	103.3(6)
N(1)–Ag(1)–P(3)	107.44(5)	107.89(10)
P(1)–Ag(1)–P(2)	114.680(14)	114.73(3)
P(1)–Ag(1)–P(3)	112.430(14)	112.12(3)
P(2)–Ag(1)–P(3)	114.821(13)	114.73(3)
Torsion angles		
P(1)–Ag(1)–N(1)–C(1)	−38.8(5)	29.0(11)
P(2)–Ag(1)–N(1)–C(1)	80.6(5)	−90.6(10)
P(3)–Ag(1)–N(1)–C(1)	−156.6(5)	147.5(10)

In summary, the reaction of the potassium salt of the *N*-thiophosphorylated thiourea Et$_2$NC(S)NHP(S)(O*i*Pr)$_2$ (**HL**) with a mixture of AgNO$_3$ and PPh$_3$ in aqueous EtOH/CH$_2$Cl$_2$ leads to the mixed-ligand silver(I) complex **[Ag(PPh$_3$)$_2$L]**. The recrystallization of the complex **[Ag(PPh$_3$)$_2$L]** from an acetone/*n*-hexane mixture leads to the decomposition of the starting complex with the formation of **[Ag(PPh$_3$)L]**, **[Ag(PPh$_3$)$_3$NCS]·(CH$_3$)$_2$C=O** and **Et$_2$NP(S)(O*i*Pr)$_2$**. According to the X-ray data, the silver(I) cation is in a NP$_3$ tetrahedral environment formed by three phosphorus atoms of the PPh$_3$ ligands and the nitrogen atom of the NCS ligand in the complex **[Ag(PPh$_3$)$_3$NCS]·(CH$_3$)$_2$C=O**. Acetone molecules are trapped in the crystal.

Acknowledgments

This work was partly funded by the Fonds National de la Recherche Scientifique-FNRS (FRFC No. 2.4508.08, IISN 4.4507.10) and the IAP INANOMAT program. We thank the F.R.S.-FNRS (Belgium) for a post-doctoral position allocated to D. A. S.

Appendix A. Supplementary material

CCDC 805545 contains the supplementary crystallographic data for **[Ag(PPh$_3$)$_3$NCS]·(CH$_3$)$_2$C=O**. 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 materials related to this article can be found online at doi:10.1016/j.inoche.2011.10.005.

References

[1] N.G. Zabirov, A.Yu. Verat, F.D. Sokolov, M.G. Babashkina, D.B. Krivolapov, V.V. Brusko, Mendeleev Communications 13 (2003) 163.
[2] A.Y. Verat, F.D. Sokolov, N.G. Zabirov, M.G. Babashkina, D.B. Krivolapov, V.V. Brusko, I.A. Litvinov, Inorganica Chimica Acta 359 (2006) 475.
[3] F.D. Sokolov, M.G. Babashkina, D.A. Safin, A.I. Rakhmatullin, F. Fayon, N.G. Zabirov, M. Bolte, V.V. Brusko, J. Galezowska, H. Kozlowski, Dalton Transactions (2007) 4693.
[4] D.A. Safin, M.G. Babashkina, T.R. Gimadiev, M. Bolte, M.V. Pinus, D.B. Krivolapov, I.A. Litvinov, Polyhedron 27 (2008) 2978.
[5] D.A. Safin, M.G. Babashkina, M. Bolte, F.D. Sokolov, V.V. Brusko, Inorganica Chimica Acta 362 (2009) 1895.

[6] F.D. Sokolov, M.G. Babashkina, F. Fayon, A.I. Rakhmatullin, D.A. Safin, T. Pape, F.E. Hahn, Journal of Organometallic Chemistry 694 (2009) 167.

[7] M.G. Babashkina, D.A. Safin, Ł. Szyrwiel, M. Kubiak, F.D. Sokolov, Y.V. Starikov, H. Kozlowski, Zeitschrift für Anorganische und Allgemeine Chemie 635 (2009) 554.

[8] R.C. Luckay, X. Sheng, C.E. Strasser, H.G. Raubenheimer, D.A. Safin, M.G. Babashkina, A. Klein, Dalton Transactions (2009) 4646.

[9] M.G. Babashkina, D.A. Safin, M. Bolte, A. Klein, CrystEngComm 12 (2010) 134.

[10] M.G. Babashkina, D.A. Safin, F. Fayon, A.I. Rakhmatullin, F.D. Sokolov, A. Klein, D.B. Krivolapov, T. Pape, F.E. Hahn, H. Kozlowski, Dalton Transactions 39 (2010) 8261.

[11] M.G. Babashkina, D.A. Safin, A. Klein, M. Bolte, European Journal of Inorganic Chemistry (2010) 4018.

[12] D.A. Safin, M.G. Babashkina, M. Bolte, M. Köckerling, Inorganica Chimica Acta 370 (2011) 59.

[13] D.A. Safin, M.G. Babashkina, F.D. Sokolov, N.G. Zabirov, J. Galezowska, H. Kozlowski, Polyhedron 26 (2007) 1113.

[14] O. Crespo, V.V. Brusko, M. Concepción Gimeno, M.L. Tornil, A. Laguna, N.G. Zabirov, European Journal of Inorganic Chemistry (2004) 423.

[15] M.G. Babashkina, D.A. Safin, A. Klein, Heteroatom Chemistry 21 (2010) 386.

[16] D.A. Safin, P.S. Mdluli, N. Revaprasadu, K. Ahmad, M. Afzaal, M. Helliwell, P. O'Brien, E.R. Shakirova, M.G. Babashkina, A. Klein, Chemistry of Materials 21 (2009) 4233.

[17] *Physical measurements*: Infrared spectra (Nujol) were recorded with a Thermo Nicolet 380 FT-IR spectrometer in the range 400–3600 cm^{-1}. NMR spectra were obtained on a Bruker Avance 300 MHz spectrometer at 25 °C. ^{1}H and ^{31}P{^{1}H} NMR spectra (CDCl$_3$) were recorded at 299.948 and 121.420 MHz, respectively. Chemical shifts are reported with reference to SiMe$_4$ (^{1}H) and 85% H$_3$PO$_4$ (^{31}P{^{1}H}). Elemental analyses were performed on a Thermoquest Flash EA 1112 Analyzer from CE Instruments. *Synthesis of* ***[Ag(PPh$_3$)$_2$L]***: A suspension of **HL** (0.156 g, 0.5 mmol) in aqueous ethanol (10 mL) was mixed with an aqueous ethanol solution (10 mL) of potassium hydroxide (0.031 g, 0.55 mmol). A mixture of AgNO$_3$ (0.085 g, 0.5 mmol) and PPh$_3$ (0.262 g, 1 mmol) in CH$_2$Cl$_2$ (20 mL) was refluxed for 0.5 h and then added dropwise under vigorous stirring to the resulting potassium salt. The mixture was stirred for an hour and the resulting precipitate of KI was filtered off and the solvent was then removed in vacuum. The residue was recrystallized from a CH$_2$Cl$_2$/*n*-hexane mixture (1:5, v/v). Isolated yield 0.406 g (86%). IR ν (cm^{-1}): 600 (P=S), 970 (POC), 1479 (SCN). ^{1}H NMR δ (ppm): 1.16 (t, $^{3}J_{H,H}$ = 6.9 Hz, 3H, CH$_3$, Et), 1.23 (t, $^{3}J_{H,H}$ = 7.0 Hz, 3H, CH$_3$, Et), 1.28 (d, $^{3}J_{H,H}$ = 6.2 Hz, 6H, CH$_3$, *i*Pr), 1.32 (d, $^{3}J_{H,H}$ = 6.2 Hz, 6H, CH$_3$, *i*Pr), 3.58 (q, $^{3}J_{H,H}$ = 7.0 Hz, 2H, CH$_2$, Et), 3.89 (q, $^{3}J_{H,H}$ = 6.9 Hz, 2H, CH$_2$, Et), 4.74 (d. sept, $^{3}J_{POCH}$ = 10.8 Hz, $^{3}J_{H,H}$ = 6.1 Hz, 2H, OCH), 7.29–7.46 (m, 30H, Ph, PPh$_3$); ^{31}P{^{1}H} NMR δ (ppm): 5.0 (2P, PPh$_3$), 52.1 (1P, NPS); *Anal.* Calc. for $C_{47}H_{54}AgN_2O_2P_3S_2$ (943.87): C 59.81, H 5.77, N 2.97. Found: C 59.70, H 5.71, N 3.02%. *Synthesis of* ***Et$_2$NP(S)(OiPr)$_2$,[Ag(PPh$_3$)$_3$NCS]·(CH$_3$)$_2$C=O,[Ag(PPh$_3$)L]***: Recrystallization of the complex **[Ag(PPh$_3$)$_2$L]** from an acetone/*n*-hexane mixture (1:3, v/v) after three days leads to the formation of the colorless crystals of **[Ag(PPh$_3$)$_3$NCS]·(CH$_3$)$_2$C=O**, which were isolated by decantation. Isolated yield 0.211 g (97%). IR ν (cm^{-1}): 793 (C=S), 1701 (C=O), 1997 (C=N). ^{1}H NMR δ (ppm): 2.10 (s, 6H, CH$_3$, acetone), 7.08–7.31 (m, Ph, PPh$_3$, overlapping with the solvent signal); ^{31}P{^{1}H} NMR δ (ppm): 4.8. *Anal.* Calc. for $C_{58}H_{51}AgNOP_3S$ (1010.90): C 68.91, H 5.09, N 1.39. Found: C 69.03, H 5.16, N 1.31%. The mother liquor was left for several days and afterwards the precipitation of colorless viscous oil of **Et$_2$NP(S)(O*i*Pr)$_2$** was observed. The product was isolated by decantation. Isolated yield 0.051 g (94%). IR ν (cm^{-1}): 611 (P=S), 722 (P–N), 984 (POC). ^{1}H NMR δ (ppm): 1.13 (t, $^{3}J_{H,H}$ = 7.0 Hz, 6H, CH$_3$, Et), 1.25 (d, $^{3}J_{H,H}$ = 6.2 Hz, 12H, CH$_3$, *i*Pr), 3.72 (q, $^{3}J_{H,H}$ = 7.0 Hz, 4H, CH$_2$, Et), 4.53 (d. sept, $^{3}J_{POCH}$ = 9.4 Hz, $^{3}J_{H,H}$ = 6.1 Hz, 2H, OCH); ^{31}P{^{1}H} NMR δ (ppm): 75.7. *Anal.* Calc. for $C_{10}H_{24}NO_2PS$ (253.34): C 47.41, H 9.55, N 5.53. Found: C 47.49, H 10.02, N 5.51%. The solvent from the mother liquor was then removed in vacuum and *n*-hexane (50 mL) was added to the resulting colorless oil, which was dissolved rapidly. The traces of the non soluble precipitate were filtered off and the solvent was then removed in vacuum. The resulting colorless oil was identified as the mixed-ligand complex **[Ag(PPh$_3$)L]**. Isolated yield 0.130 g (89%). IR ν (cm^{-1}): 596 (P=S), 981 (POC), 1521 (SCN). ^{1}H NMR δ (ppm): 1.13 (t, $^{3}J_{H,H}$ = 6.8 Hz, 3H, CH$_3$, Et), 1.27 (t, $^{3}J_{H,H}$ = 6.9 Hz, 3H, CH$_3$, Et), 1.23 (d, $^{3}J_{H,H}$ = 6.0 Hz, 6H, CH$_3$, *i*Pr), 1.34 (d, $^{3}J_{H,H}$ = 6.1 Hz, 6H, CH$_3$, *i*Pr), 3.64 (q, $^{3}J_{H,H}$ = 6.9 Hz, 2H, CH$_2$, Et), 3.93 (q, $^{3}J_{H,H}$ = 6.9 Hz, 2H, CH$_2$, Et), 4.89 (d. sept, $^{3}J_{POCH}$ = 10.2 Hz, $^{3}J_{H,H}$ = 6.0 Hz, 2H, OCH), 7.37–7.50 (m, 15H, Ph, PPh$_3$); ^{31}P{^{1}H} NMR δ (ppm): 4.7 (1P, PPh$_3$), 50.4 (1P, NPS); *Anal.* Calc. for $C_{29}H_{39}AgN_2O_2P_2S_2$ (681.58): C 51.10, H 5.77, N 4.11. Found: C 51.19, H 5.82, N 4.06%.

[18] R.C. Luckay, X. Sheng, C.E. Strasser, H.G. Raubenheimer, D.A. Safin, M.G. Babashkina, A. Klein, Dalton Transactions (2009) 8227.

[19] A.H. Othman, H.-K. Fun, K. Sivakumar, Y. Farina, I. Baba, Acta Crystallographica C52 (1996) 1933.

[20] H.R. Phillips, D.J. Williams, A.M.Z. Slawin, J.D. Wollins, Polyhedron 15 (1996) 3725.

[21] R.N. Dash, D.V. Ramana Rao, Zeitschrift für Anorganische und Allgemeine Chemie 393 (1972) 309.

[22] J.L. Cox, J. Howatson, Inorganic Chemistry 12 (1973) 1205.

[23] B. Kaboudin, M. Karimi, H. Zahedi, Organic Preparations and Procedures International 40 (2008) 399.

[24] The X-ray diffraction data for the crystal of **[Ag(PPh$_3$)$_3$NCS]·(CH$_3$)$_2$C=O** were collected on a STOE IPDS-II diffractometer. The images were indexed, integrated and scaled using the X-Area package [25]. Data were corrected for absorption using the PLATON program [26]. The structures were solved by direct methods using the SHELXS program [27] and refined first isotropically and then anisotropically using SHELXL97 [27]. Hydrogen atoms were revealed from $\Delta\rho$ maps and refined using a riding model. The figure was generated using the program Mercury [28].

[25] Stoe & Cie, X-Area. Area-Detector Control and Integration Software, Stoe & Cie, Darmstadt, Germany, 2001.

[26] A.L. Spek, Journal of Applied Crystallography 36 (2003) 7.

[27] G.M. Sheldrick, Acta Crystallographica A64 (2008) 112.

[28] I.J. Bruno, J.C. Cole, P.R. Edgington, M. Kessler, C.F. Macrae, P. McCabe, J. Pearson, R. Taylor, Acta Crystallographica. Section B, Structural Science 58 (2002) 389.