Silver(I) complexes of *N*-thiophosphorylated bis(iminophosphorane) ligands: From monomers to polymers†

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Received 6th March 2007, Accepted 9th May 2007
First published as an Advance Article on the web 22nd May 2007
DOI: 10.1039/b703348f

Treatment of diphosphines $Ph_2P(CH_2)_nPPh_2$ ($n = 1, 2, 4, 6$) and $[Fe(\eta^5\text{-}C_5H_4PR'_2)_2]$ ($R' = Ph, {}^iPr$) with a two-fold excess of $(RO)_2P(=S)N_3$ ($R = Et, Ph$) results in the high-yield formation of the *N*-thiophosphorylated bis(iminophosphorane) derivatives $(CH_2)_n[P\{=NP(=S)(OR)_2\}Ph_2]_2$ and $Fe(\eta^5\text{-}C_5H_4[P\{=NP(=S)(OR)_2\}R'_2])_2$, respectively. The reactions of these ligands with $AgSbF_6$ in a 1 : 1 molar ratio have been investigated. The resulting silver(I) complexes, derived from the selective coordination of the P=S units, have been characterized by IR, NMR and MS (FAB) spectroscopy and, in selected cases, by X-ray crystallography. Monomeric, dimeric and polymeric solid-state structures, depending on the nature of the ligand backbone, have been found.

Introduction

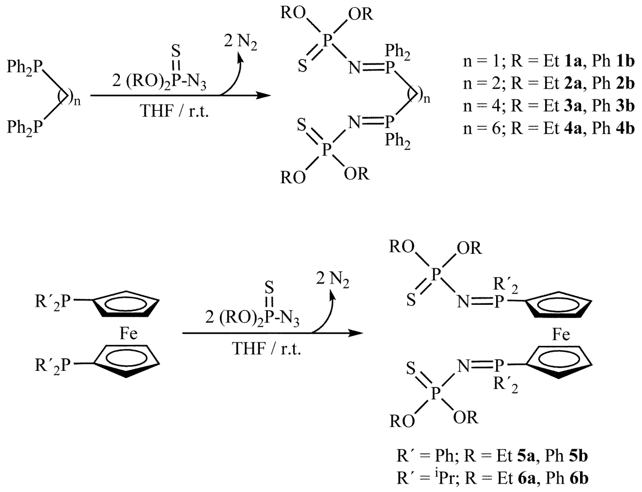
N-Thiophosphorylated iminophosphoranes of general composition $R_3P{=}N{-}P(=S)(OR')_2$, readily accessible *via* Staudinger-type reactions between phosphines PR_3 and azides $(R'O)_2P(=S)N_3$,[1] have received a great deal of synthetic interest during the last years. In particular, Caminade and Majoral and co-workers have demonstrated that such structural units can be used for the construction of a variety of phosphorus-containing macrocycles (*i.e.* cryptands and spherands)[2] and dendrimers.[3] Moreover, the ability of compounds $R_3P{=}N{-}P(=S)(OR')_2$ to undergo regioselective electrophilic additions at the sulfur atom is also well-documented.[4] In contrast, little is known on the coordination chemistry of *N*-thiophosphorylated iminophosphoranes. Thus, to the best of our knowledge, only a few Au(I) and Cu(I) complexes, derived from the selective coordination of the sulfur atom to the metal, have been reported to date.[5,6]

Herein we report the high-yield preparation of the novel *N*-thiophosphorylated bis(iminophosphorane) ligands $(CH_2)_n[P\{=NP(=S)(OR)_2\}Ph_2]_2$ ($n = 2, 4, 6$; $R = Et, Ph$) and $Fe(\eta^5\text{-}C_5H_4[P\{=NP(=S)(OR)_2\}R'_2])_2$ ($R = Et, Ph$; $R' = Ph, {}^iPr$), *via* Staudinger-type reactions between the corresponding bis(diphenylphosphino)alkane $Ph_2P(CH_2)_nPPh_2$ or ferrocenyl-diphosphine $Fe(\eta^5\text{-}C_5H_4PR'_2)_2$, respectively, and phosphorylated azides $(RO)_2P(=S)N_3$. The behaviour of these ligands towards $AgSbF_6$ has been studied allowing the preparation of the first Ag(I) complexes containing coordinated P=N–P=S units. Remarkably, solid state X-ray structural characterization of some of these Ag(I) complexes, in which the ligands are selectively coordinated through the sulfur atoms, points out that their nuclearity (monomeric, dimeric or polymeric) is strongly dependent on the nature of the diphosphine backbone.

Results and discussion

Synthesis and characterization of *N*-thiophosphorylated bis(iminophosphorane) ligands 1–6a,b

Following the experimental procedure previously used by us for the preparation of $CH_2[P\{=NP(=S)(OR)_2\}Ph_2]_2$ (R = Et **1a**, Ph **1b**),[6c] the novel *N*-thiophosphorylated bis(iminophosphorane) ligands $(CH_2)_n[P\{=NP(=S)(OR)_2\}Ph_2]_2$ (*n* = 2, R = Et **2a**, Ph **2b**; *n* = 4, R = Et **3a**, Ph **3b**; *n* = 6, R = Et **4a**, Ph **4b**) have been readily synthesized by treatment of the appropriate bis(diphenylphosphino)alkane with the phosphorylated azides $(RO)_2P(=S)N_3$ (R = Et, Ph) (see Scheme 1).[7a] In a similar way, Staudinger-type reactions between these functionalized azides and the ferrocenyl-diphosphines $[Fe(\eta^5\text{-}C_5H_4PR'_2)_2]$ (R′ = Ph (dppf), ${}^iPr$ (dippf)) result in the clean formation of compounds **5–6a**,**b** (Scheme 1).[7b]



Scheme 1 Synthesis of the bis(iminophosphorane) ligands **1–6a**,**b**.

Compounds **2–6a**,**b**, isolated as air-stable white (**2–4a**,**b**) or yellow (**5–6a**,**b**) solids in 83–94% yield, have been characterized by IR and NMR spectroscopy ($^{31}P\text{–}\{^1H\}$, ^1H and $^{13}C\text{–}\{^1H\}$) as

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† CCDC reference numbers 639179–639183. For crystallographic data in CIF or other electronic format see DOI: 10.1039/b703348f

Table 1 ^{31}P–{^{1}H} NMR data for the ligands **1–6a**,**b** and their silver(I) complexes **7–12a**,**b**^{a}

Ligand	$R_2P{=}N$	$(RO)_2P{=}S$	^2J(PP)	Complex	$R_2P{=}N$	$(RO)_2P{=}S$	^2J(PP)
1a^b	9.14 (m)^{d,e}	59.07 (m)^{d,e}	—	**7a**^{b}	11.88 (m)^d	54.34 (m)^d	—
1b^b	10.95 (m)^{d,e}	51.23 (m)^{d,e}	—	**7b**^{c}	13.37 (m)^d	48.00 (m)^d	—
2a^b	17.52 (m)^d	59.69 (m)^d	—	**8a**^{b}	20.83 (m)^d	51.38 (m)^d	—
2b^b	19.78 (m)^d	52.64 (m)^d	—	**8b**^{c}	23.67 (m)^d	48.85 (m)^d	—
3a^b	18.34 (d)	60.47 (d)	33.4	**9a**^{b}	21.37 (d)	51.85 (d)	20.0
3b^b	19.72 (d)	52.78 (d)	35.2	**9b**^{c}	23.04 (d)	46.01 (d)	28.9
4a^b	18.44 (d)	60.68 (d)	32.5	**10a**^{c}	20.65 (d)	52.57 (d)	12.5
4b^b	19.95 (d)	52.88 (d)	35.1	**10b**^{b}	23.16 (d)	45.43 (d)	23.5
5a^b	12.59 (d)	59.48 (d)	31.0	**11a**^{b}	17.72 (d)	55.59 (d)	12.1
5b^b	14.82 (d)	51.17 (d)	32.5	**11b**^{c}	19.30 (d)	46.11 (d)	18.0
6a^b	34.38 (d)	56.49 (d)	29.3	**12a**^{b}	39.95 (d)	45.86 (d)	11.7
6b^b	37.43 (d)	48.64 (d)	31.7	**12b**^{c}	41.30 (d)	42.36 (d)	22.6

^{a} δ in ppm and J in Hz. ^{b} Spectra recorded in $CDCl_3$. ^{c} Spectra recorded in CD_2Cl_2. ^{d} AA′XX′ spin system. ^{e} Data taken from reference 6*c*.

well as elemental analyses, all data being fully consistent with the proposed formulations (details are given in the Experimental section). In particular, the ^{31}P–{^{1}H} NMR spectra are very informative (see Table 1), showing the presence of two well-separated signals at δ_P 10.95–19.95 ($Ph_2P{=}N$)[8] and 48.64–60.68 ($(RO)_2P{=}S$) ppm, the chemical shifts observed being characteristic of *N*-thiophosphorylated iminophosphorane chains $–Ph_2P{=}N–P({=}S)(OR)_2$.[4–6] It should be also noted that while the spectra of compounds **3–6a**,**b** display a typical AB pattern (^2J(PP) = 29.3–35.2 Hz), for **2a**,**b** two unresolved multiplets, consistent with an AA′XX′ spin system, are found (see Table 1). This fact, previously observed for **1a**,**b**,[6c] clearly indicates that J_{PP} couplings between the iminophosphorane units take place when short diphosphine spacers are present in these *N*-thiophosphorylated bis(iminophosphoranes).

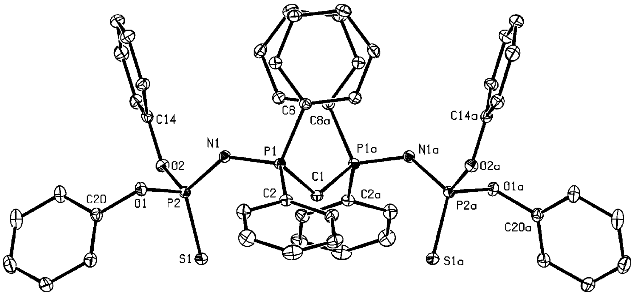
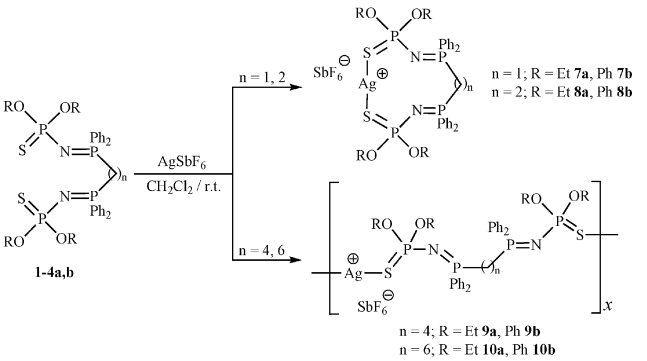


Fig. 1 ORTEP-type view of the structure of compound **1b** showing the crystallographic labeling scheme. Atoms labeled with an "a" are related to those indicated by a crystallographic 2-fold symmetry axis. Hydrogen atoms have been omitted for clarity. Thermal ellipsoids are drawn at 10% probability level. Selected bond lengths (Å): C(1)–P(1) = 1.816(2); P(1)–N(1) = 1.574(2); N(1)–P(2) = 1.579(2); P(2)–S(1) = 1.9319(11); P(2)–O(1) = 1.605(2); P(2)–O(2) = 1.601(2). Selected bond angles (°): P(1)–C(1)–P(1a) = 123.2(2); C(1)–P(1)–N(1) = 113.07(9); P(1)–N(1)–P(2) = 133.20(16); N(1)–P(2)–S(1) = 121.58(10); N(1)–P(2)–O(1) = 102.07(12); N(1)–P(2)–O(2) = 107.82(12).

For comparative purposes (see below), the molecular structure of one of these ligands, *i.e.* the previously reported derivative $CH_2[P\{{=}NP({=}S)(OPh)_2\}Ph_2]_2$ (**1b**),[6c] has been determined by means of single-crystal X-ray diffraction methods. An ORTEP plot is shown in Fig. 1; selected bonding parameters are listed in the caption. As previously observed in other species containing related *N*-thiophosphorylated iminophosphorane units $–Ph_2P{=}N–P({=}S)(OR)_2$,[4g,9] the lengths of the formal single and double PN bonds were found to be almost identical (P(1)–N(1) = 1.574(2) Å *vs* N(1)–P(2) = 1.579(2) Å). This fact clearly reflects an extensive electronic delocalization of the nitrogen lone pair across the P=N–P=S frameworks in this molecule. The P(2)–S(1) distance (1.9319(11) Å) is also classical for this type of compound.[4g,9]

Silver(I) complexes containing the *N*-thiophosphorylated bis(iminophosphorane)alkane ligands 1–4a,b

Treatment of dichloromethane solutions of the bis(iminophosphorane)-methane or ethane ligands **1–2a**,**b** with 1 equivalent of silver hexafluoroantimonate results in the high-yield formation (81–87%) of the mononuclear chelate complexes $[Ag\{\kappa^2(S,S')\text{-}(CH_2)_n[P\{{=}NP({=}S)(OR)_2\}Ph_2]_2\}][SbF_6]$ (n = 1, R = Et **7a**, Ph **7b**; n = 2, R = Et **8a**, Ph **8b**) *via* selective *S*-coordination of the *N*-thiophosphoryl-iminophosphoranyl fragments (Scheme 2). In contrast, the reactions of the bis(iminophosphorane) ligands **3–4a**,**b**, containing longer hydrocarbonated chains, with $AgSbF_6$ generate, under the same conditions, the polymeric derivatives $[Ag\{(CH_2)_n[P\{{=}NP({=}S)(OR)_2\}Ph_2]_2\}]_x[SbF_6]_x$ (n = 4, R = Et **9a**, Ph **9b**; n = 6, R = Et **10a**, Ph **10b**) (77–88% yield; Scheme 2).



Scheme 2 Synthesis of the silver(I) complexes **7–10a**,**b**.

Compounds **7–10a**,**b** have been isolated as air- and moisture-stable white solids that behave as 1 : 1 electrolytes in acetone solutions (Λ_M = 108–128 Ω^{-1} cm^2 mol^{-1}). The complexation of ligands **1–4a**,**b** to silver is reflected in the ^{31}P–{^{1}H} NMR spectra of compounds **7–10a**,**b** by slight shifts of the $Ph_2P{=}N$

and $(RO)_2P{=}S$ resonances, *i.e.* to downfield ($\Delta\delta = 2$ to 5 ppm) for the former and to highfield for the latter ($\Delta\delta = -3$ to -10 ppm) (see Table 1). A similar trend has been previously reported in the *S*-coordination of related $-Ph_2P{=}N{-}P({=}S)(OR)_2$ units to Au(I) and Cu(I) fragments,[5] suggesting that silver-complexation takes place selectively on the P=S *vs* P=N groups. Although the formation of formally 1 : 1 adducts of the starting reagents [$AgSbF_6$·ligand] is readily deduced from their elemental analyses and FAB mass spectra (details are given in the Experimental section), the real nature of these complexes could only be determined by single-crystal X-ray diffraction methods. Drawings of the molecular structure of **7a**, **8b** and **9a** along with selected bonding parameters are shown in Fig. 2, 3 and 4, respectively.

Concerning the structure of complex **7a** (see Fig. 2), the X-ray analysis unambiguously confirms the formation of a ten-membered chelate ring, as suggested by the $^{31}P{-}\{^1H\}$ NMR data, the bis(iminophosphorane) ligand **1a** being coordinated to silver through the $(EtO)_2P{=}S$ units. The Ag(1)–S(1) (2.435(2) Å) and Ag(1)–S(2) (2.449(2) Å) bond lengths compare well with those shown by Ag(I) complexes containing *S*-coordinated phosphine-sulfides.[10] Remarkably, intermolecular silver–sulfur interactions take place in the solid state leading to a dimeric centrosymmetric structure.[11] The Ag(1)–S(2a) distance of 2.870(2) Å can be reasonably regarded as a real bonding interaction since it falls within the accepted range for single Ag–S bonds (*ca.* 2.2–3.0 Å).[10d] A weak silver–silver contact is also present in the dimer (Ag(1)–Ag(1a) = 3.138(2) Å).[12] The existence of all these intermolecular bonding interactions is clearly reflected in the S(1)–Ag(1)–S(2) angle which deviates considerably from the expected linearity (159.21(6)°). It is also interesting to note that bond distances within the P=N–P=S frameworks are almost identical (*ca.* ±0.07 Å) to those found in the structure of the free ligand **1b** (Fig. 1), indicating that electronic delocalization of the nitrogen lone pair is maintained upon coordination of the thiophosphoryl unit to the metal.

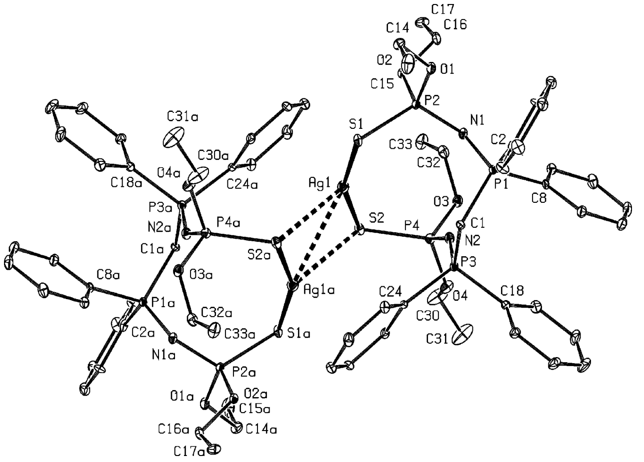


Fig. 2 ORTEP-type view of the structure of compound **7a** showing the crystallographic labeling scheme. Atoms labeled with an "a" are related to those indicated by a crystallographic center of symmetry. Hydrogen atoms and SbF_6^- anions have been omitted for clarity. Thermal ellipsoids are drawn at 10% probability level. Selected bond lengths (Å): Ag(1)–S(1) = 2.435(2); Ag(1)–S(2) = 2.449(2); Ag(1)–S(2a) = 2.870(2); Ag(1)–Ag(1a) = 3.138(2); C(1)–P(1) = 1.824(6); P(1)–N(1) = 1.570(5); N(1)–P(2) = 1.594(5); P(2)–S(1) = 1.993(2); C(1)–P(3) = 1.812(6); P(3)–N(2) = 1.563(5); N(2)–P(4) = 1.556(5); P(4)–S(2) = 2.004(2). Selected bond angles (°): S(1)–Ag(1)–S(2) = 159.21(6); S(1)–Ag(1)–S(2a) = 87.74(5); S(1)–Ag(1)–Ag(1a) = 133.91(5); S(2)–Ag(1)–S(2a) = 108.19(5); S(2)–Ag(1)–Ag(1a) = 60.34(4); S(2a)–Ag(1)–Ag(1a) = 47.85(4); P(1)–C(1)–P(3) = 116.1(3); C(1)–P(1)–N(1) = 112.8(3); P(1)–N(1)–P(2) = 130.2(3); N(1)–P(2)–S(1) = 118.2(2); P(2)–S(1)–Ag(1) = 100.35(8); C(1)–P(3)–N(2) = 109.8(3); P(3)–N(2)–P(4) = 146.0(4); N(2)–P(4)–S(2) = 116.8(2); P(4)–S(2)–Ag(1) = 98.52(8); P(4)–S(2)–Ag(1a) = 120.27(9); Ag(1)–S(2)–Ag(1a) = 71.81(5).

As shown in Fig. 3, complex **8b** remains monomeric in the solid state, the absence of intermolecular Ag–S interactions leading in this case to an almost linear geometry around the silver atom (S(1)–Ag(1)–S(2) = 171.74(4)°) with slightly shorter Ag(1)–S(1) (2.3977(11) Å) and Ag(1)–S(2) (2.4036(11) Å) bond lengths. The rest of the distances within the 11-membered chelate ring compare well with those found in the dimeric structure of complex **7a**.

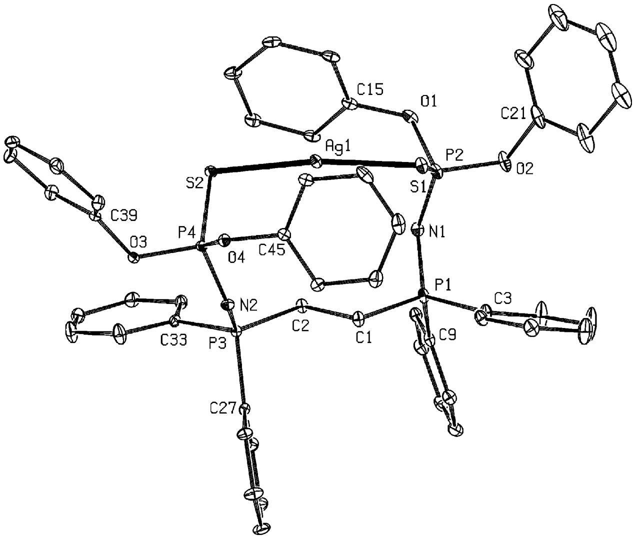


Fig. 3 ORTEP-type view of the structure of compound **8b** showing the crystallographic labeling scheme. Hydrogen atoms, SbF_6^- anions and the half-occupancy dichloromethane molecule of solvation have been omitted for clarity. Thermal ellipsoids are drawn at 10% probability level. Selected bond lengths (Å): Ag(1)–S(1) = 2.3977(11); Ag(1)–S(2) = 2.4036(11); C(1)–P(1) = 1.819(4); P(1)–N(1) = 1.584(4); N(1)–P(2) = 1.580(4); P(2)–S(1) = 1.9850(15); C(2)–P(3) = 1.811(4); P(3)–N(2) = 1.584(4); N(2)–P(4) = 1.572(4); P(4)–S(2) = 1.9811(14). Selected bond angles (°): S(1)–Ag(1)–S(2) = 171.74(4); C(1)–P(1)–N(1) = 110.9(2); P(1)–N(1)–P(2) = 129.0(2); N(1)–P(2)–S(1) = 119.01(15); P(2)–S(1)–Ag(1) = 98.01(5); P(1)–C(1)–C(2) = 111.0(3); C(1)–C(2)–P(3) = 112.2(3); C(2)–P(3)–N(2) = 114.5(2); P(3)–N(2)–P(4) = 135.1(2); N(2)–P(4)–S(2) = 119.34(15); P(4)–S(2)–Ag(1) = 98.59(5).

In contrast to **7a** and **8b**, the solid-state structure of complex **9a** is a one-dimensional zigzag polymer (see Fig. 4), the *N*-thiophosphorylated bis(iminophosphorane) unit acting as a bridging ligand between two silver atoms.[13,14] The asymmetric unit corresponds to the fragment [$\{CH_2CH_2Ph_2P{=}NP({=}S)(OEt)_2\}_2Ag$], which gives rise the polymeric chain *via* pairs of inversion centres. The coordination around the silver atom is slightly distorted from linearity (S(1)–Ag(1)–S(2) = 167.99(10)°) with Ag(1)–S(1) and Ag(1)–S(2) bond lengths of 2.324(3) and 2.376(4) Å, respectively.

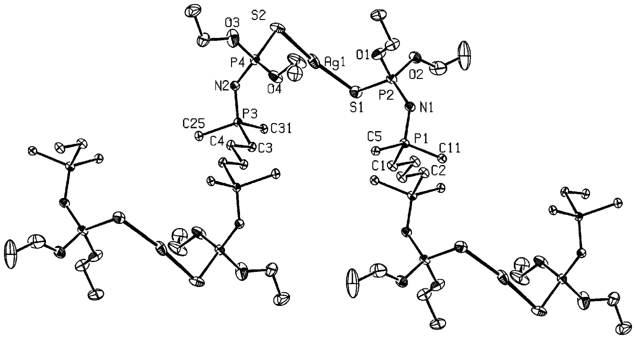
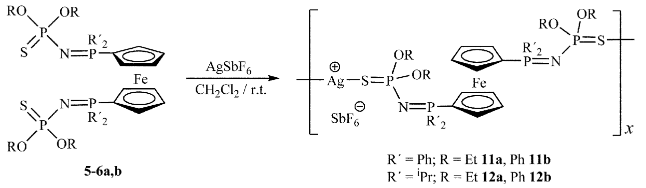


Fig. 4 Part of the polymeric chain of complex **9a** showing the crystallographic labeling scheme. Hydrogen atoms, aryl groups (except the *ipso* carbons) and SbF_6^- anions have been omitted for clarity. Thermal ellipsoids are drawn at 10% probability level. Selected bond lengths (Å): Ag(1)–S(1) = 2.324(3); Ag(1)–S(2) = 2.376(4); C(1)–P(1) = 1.792(6); P(1)–N(1) = 1.571(6); N(1)–P(2) = 1.566(6); P(2)–S(1) = 1.990(3); C(3)–P(3) = 1.804(6); P(3)–N(2) = 1.571(6); N(2)–P(4) = 1.563(6); P(4)–S(2) = 1.978(3). Selected bond angles (°): S(1)–Ag(1)–S(2) = 167.99(10); C(1)–P(1)–N(1) = 114.7(3); P(1)–N(1)–P(2) = 137.0(4); N(1)–P(2)–S(1) = 116.0(2); P(2)–S(1)–Ag(1) = 103.12(2); P(1)–C(1)–C(2) = 112.7(4); C(4)–P(3)–N(2) = 114.9(3); P(3)–N(2)–P(4) = 138.1(4); N(2)–P(4)–S(2) = 117.5(2); P(4)–S(2)–Ag(1) = 100.90(12).

Silver(I) complexes containing the *N*-thiophosphorylated ferrocenyl ligands 5–6a,b

The reactivity of the ferrocenyl derivatives $Fe(\eta^5\text{-}C_5H_4[P\{=NP(=S)(OR)_2\}Ph_2])_2$ (R = Et **5a**, Ph **5b**) and $Fe(\eta^5\text{-}C_5H_4[P\{=NP(=S)(OR)_2\}{}^iPr_2])_2$ (R = Et **6a**, Ph **6b**) towards silver hexafluoroantimonate has also been explored, the treatment, at room temperature, of a dichloromethane solution of these ligands with 1 equiv. of $AgSbF_6$ leading to the high-yield formation (79–86%) of the polymeric species $[Ag\{Fe(\eta^5\text{-}C_5H_4[P\{=NP(=S)(OR)_2\}Ph_2])_2\}]_x[SbF_6]_x$ (R = Et **11a**, Ph **11b**) and $[Ag\{Fe(\eta^5\text{-}C_5H_4[P\{=NP(=S)(OR)_2\}{}^iPr_2])_2\}]_x[SbF_6]_x$ (R = Et **12a**, Ph **12b**) in which the bis(iminophosphorane) units bridge two Ag atoms *via* selective *S*-coordination (Scheme 3).

The characterization of complexes **11–12a**,**b**, isolated as air- and moisture-stable yellow-orange solids, was achieved by means of elemental analyses, conductance measurements (1 : 1 electrolytes; $\Lambda_M = 108\text{–}116\ \Omega^{-1}\ cm^2\ mol^{-1}$), positive-ion FAB mass spectra (in all cases the cation molecular peak $[Ag/ligand + 1]^+$ is observed (50–100% intensity)) and multinuclear ($^{31}P\text{–}\{^1H\}$, ^1H and $^{13}C\text{–}\{^1H\}$) NMR spectroscopy (details are given in the Experimental section). In particular, the silver complexation to sulfur is easily detected by $^{31}P\text{–}\{^1H\}$ NMR, which displays phenomena analogous to those observed for **7–10a**,**b**, *i.e.* the signal corresponding to the iminophosphorane unit is deshielded ($\Delta\delta$ = 4 to 5 ppm) whereas the $(RO)_2P{=}S$ phosphorus resonance is shielded ($\Delta\delta$ = −4 to −11 ppm) when compared to the free ligands (see Table 1). The polymeric nature of these species was ascertained by means of an X-ray diffraction analysis on complex **11b**.[14] The ORTEP view of the polymeric chain, along with selected structural parameters, is shown in Fig. 5. In this case, the asymmetric unit consists of the $[Ag_2\{\mu\text{-}Fe(\eta^5\text{-}C_5H_4[P\{=NP(=S)(OPh)_2\}Ph_2])_2\}]$ moiety, the two independent silver atoms each lie on inversion centres resulting in exactly 180° ideal linear geometry at Ag(1) and Ag(2). Concerning the ferrocene moiety, the cyclopentadienyl rings are staggered by 19° about the Cp · · · Cp axis as defined by the torsion angle C(25)–C*–C**–C(30).



Scheme 3 Synthesis of the ferrocenyl-based polymers **11–12a**,**b**.

Conclusions

A new family of *N*-thiophosphorylated iminophosphoranes, namely $(CH_2)_n[P\{=NP(=S)(OR)_2\}Ph_2]_2$ (R = Et, Ph; n = 1, 2, 3, 4) and $Fe(\eta^5\text{-}C_5H_4[P\{=NP(=S)(OR)_2\}R'_2])_2$ (R = Et, Ph; R′ = Ph, ^{i}Pr) has been easily synthesized from the corresponding bis(diphenylphosphino)alkane $Ph_2P(CH_2)_nPPh_2$ or ferrocenyl-diphosphine $Fe(\eta^5\text{-}C_5H_4PR'_2)_2$, respectively, and phosphorylated azides $(RO)_2P(=S)N_3$. The ability of these species to act as ligands has been also demonstrated, the complexation of their P=N–P=S linkages to silver taking place selectively through the sulfur atom. Solid state X-ray structural characterization of some of the Ag(I) complexes synthesized points out that their nuclearity is strongly dependent on the nature of the diphosphine backbone. Thus, the formation of mononuclear complexes, *via* chelation of the ligand, has been only observed when short hydrocarbonated P–X–P spacers are present (X = CH_2, CH_2CH_2), otherwise one-dimensional polymeric chains are formed.

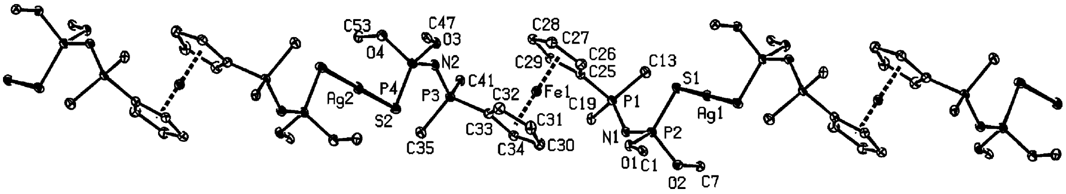


Fig. 5 Part of the polymeric chain of complex **11b** showing the crystallographic labeling scheme. Hydrogen atoms, aryl groups (except the *ipso* carbons) and SbF_6^- anions have been omitted for clarity. Thermal ellipsoids are drawn at 20% probability level. Selected bond lengths (Å): Ag(1)–S(1) = 2.3657(17); Ag(2)–S(2) = 2.3740(17); C(25)–P(1) = 1.783(7); P(1)–N(1) = 1.592(5); N(1)–P(2) = 1.572(5); P(2)–S(1) = 1.982(2); C(35)–P(3) = 1.804(7); P(3)–N(2) = 1.595(6); N(2)–P(4) = 1.564(5); P(4)–S(2) = 1.983(2); Fe(1)–C* = 1.6525(10); Fe(1)–C** = 1.6414(10). Selected bond angles (°): S(1)–Ag(1)–S(1a) = 180; S(2)–Ag(2)–S(2a) = 180; C(25)–P(1)–N(1) = 114.1(3); P(1)–N(1)–P(2) = 130.9(4); N(1)–P(2)–S(1) = 115.3(2); P(2)–S(1)–Ag(1) = 105.77(9); C(35)–P(3)–N(2) = 114.8(3); P(3)–N(2)–P(4) = 132.3(4); N(2)–P(4)–S(2) = 116.9(2); P(4)–S(2)–Ag(2) = 100.11(8); C*–Fe(1)–C** = 176.63(7). C* and C** = centroids of the cyclopentadienyl rings (C(25), C(26), C(27), C(28), C(29) and C(30), C(31), C(32), C(33), C(34), respectively).

Experimental

General comments

All manipulations were performed under an atmosphere of dry nitrogen using vacuum-line and standard Schlenk techniques. Solvents were dried by standard methods and distilled under nitrogen before use. All reagents were obtained from commercial suppliers and used without further purification with the exception of compounds $(RO)_2P(=S)N_3$ (R = Et, Ph),[15] dppf,[16] dippf,[17] and $CH_2[P\{=NP(=S)(OR)_2\}Ph_2]_2$ (R = Et **1a**, Ph **1b**)[6c] which were prepared by following the methods described in the literature. Infrared spectra were recorded on a Perkin-Elmer 1720-XFT or a Perkin-Elmer 599 spectrometer. The conductivities were measured at room temperature, in *ca.* 10^{-3} mol dm^{-3} acetone solutions, with a Jenway PCM3 conductimeter. Mass spectra (FAB) were recorded using a VG Autospec spectrometer, operating in the positive mode; 3-nitrobenzylalcohol was used as the matrix. The C, H and N analyses were carried out with a Perkin-Elmer 2400 microanalyzer. NMR spectra were recorded on a Bruker DPX300 instrument at 300 MHz (^{1}H), 121.5 MHz (^{31}P) or 75.4 MHz (^{13}C) using $SiMe_4$ or 85% H_3PO_4 as standards. DEPT experiments have been carried out for all the compounds reported in this paper.

Preparations

$(CH_2)_n[P\{=NP(=S)(OR)_2\}Ph_2]_2$ (*n* = 2, R = Et 2a, Ph 2b; *n* = 4, R = Et 3a, Ph 3b; *n* = 6, R = Et 4a, Ph 4b). A solution of the corresponding diphosphine $Ph_2P(CH_2)_nPPh_2$ (*n* = 2, 4, 6; 1 mmol) in tetrahydrofuran (20 cm^3) was treated at room temperature with the appropriate azide $(RO)_2P(=S)N_3$ (R = Et, Ph; 2.2 mmol) for 10 h. The solvent was then removed under reduced pressure to give a colorless oil which was washed with *n*-pentane (3 × 10 cm^3) and dried *in vacuo* to afford compounds **2–4a**,**b** as air-stable white solids.

***2a*.** Yield: 0.630 g, 86% (Found: C, 55.66; H, 5.98; N, 3.91. $C_{34}H_{44}O_4P_4N_2S_2$ requires C, 55.73; H, 6.05; N, 3.82%); ν_{max}/cm^{-1} (KBr) 488w, 513m, 526s, 622w, 674m, 695s, 722s, 746s, 768s, 789m, 832m, 932s, 957s, 1036vs, 1120s, 1185w, 1271s, 1290s, 1388w, 1438m, 1484w, 1589w, 2896m, 2943w, 2977m; δ_H ($CDCl_3$) 1.21 (t, 12H, ^3J(HH) = 7.2 Hz, CH_3), 3.15 (br, 4H, PCH_2), 4.00 (m, 8H, OCH_2), 7.28–7.52 (m, 12H, Ph), 7.84–7.95 (m, 8H, Ph); δ_C ($CDCl_3$) 15.98 (d, ^3J(CP) = 8.6 Hz, CH_3), 21.05 (m, PCH_2), 61.99 (d, ^2J(CP) = 5.9 Hz, OCH_2), 128.68 (d, ^3J(CP) = 13.0 Hz, *m*-Ph), 128.95 (dd, ^1J(CP) = 107.2 Hz, ^3J(CP) = 5.6 Hz, *i*-Ph), 131.53 (d, ^2J(CP) = 10.7 Hz, *o*-Ph), 132.23 (s, *p*-Ph).

***2b*.** Yield: 0.814 g, 88% (Found: C, 65.12; H, 4.86; N, 3.12. $C_{50}H_{44}O_4P_4N_2S_2$ requires C, 64.93; H, 4.79; N, 3.03%); ν_{max}/cm^{-1} (KBr) 487w, 519m, 605w, 690s, 723m, 737s, 781s, 839m, 890s, 911s, 926s, 1023w, 1115m, 1177m, 1194vs, 1259m, 1437w, 1487s, 1588m, 2909w, 2951w, 3055w; δ_H ($CDCl_3$) 2.88 (br, 4H, PCH_2), 7.09–7.25 (m, 20H, Ph), 7.42–7.69 (m, 20H, Ph); δ_C ($CDCl_3$) 20.54 (m, PCH_2), 122.24 (d, ^3J(CP) = 4.8 Hz, *o*-OPh), 124.80 (s, *p*-OPh), 128.48 (dd, ^1J(CP) = 117.3 Hz, ^3J(CP) = 5.4 Hz, *i*-Ph), 129.35 (d, ^3J(CP) = 12.5 Hz, *m*-Ph), 129.56 (s, *m*-OPh), 132.19 (d, ^2J(CP) = 10.2 Hz, *o*-Ph), 133.04 (s, *p*-Ph), 152.46 (d, ^2J(CP) = 9.7 Hz, *i*-OPh).

***3a*.** Yield: 0.700 g, 92% (Found: C, 56.95; H, 6.17; N, 3.66. $C_{36}H_{48}O_4P_4N_2S_2$ requires C, 56.83; H, 6.36; N, 3.68%); ν_{max}/cm^{-1} (KBr) 488m, 512w, 544s, 618m, 683m, 694s, 717s, 755s, 776s, 797s, 818s, 852m, 959s, 999w, 1045vs, 1103w, 1118s, 1186m, 1232vs, 1287w, 1387m, 1439s, 1484m, 1590w, 2922w, 2982m, 3050w; δ_H ($CDCl_3$) 1.23 (t, 12H, ^3J(HH) = 6.6 Hz, CH_3), 1.79 (m, 4H, CH_2), 2.82 (m, 4H, PCH_2), 4.00 (m, 8H, OCH_2), 7.30–7.59 (m, 12H, Ph), 7.75–7.82 (m, 8H, Ph); δ_C ($CDCl_3$) 15.97 (d, ^3J(CP) = 8.5 Hz, CH_3), 22.29 (dd, ^3J(CP) = 17.5 Hz, ^2J(CP) = 3.0 Hz, CH_2), 26.04 (d, ^1J(CP) = 65.1 Hz, PCH_2), 61.77 (d, ^2J(CP) = 6.3 Hz, OCH_2), 128.56 (d, ^3J(CP) = 12.3 Hz, *m*-Ph), 129.83 (dd, ^1J(CP) = 105.0 Hz, ^3J(CP) = 5.9 Hz, *i*-Ph), 131.29 (d, ^2J(CP) = 10.0 Hz, *o*-Ph), 131.99 (d, ^4J(CP) = 2.2 Hz, *p*-Ph).

***3b*.** Yield: 0.791 g, 83% (Found: C, 65.43; H, 5.14; N, 3.07. $C_{52}H_{48}O_4P_4N_2S_2$ requires C, 65.54; H, 5.08; N, 2.94%); ν_{max}/cm^{-1} (KBr) 485m, 516m, 529m, 619w, 689s, 717m, 739s, 762s, 774s, 847m, 898s, 907s, 997w, 1023m, 1069w, 1113s, 1158s, 1200vs, 1240m, 1274s, 1437m, 1453w, 1487s, 1592s, 2926w, 2944w, 3038w, 3055w; δ_H ($CDCl_3$) 1.57 (m, 4H, CH_2), 2.66 (m, 4H, PCH_2), 7.12–7.30 (m, 20H, Ph), 7.45–7.67 (m, 20H, Ph); δ_C ($CDCl_3$) 22.52 (dd, ^3J(CP) = 18.5 Hz, ^2J(CP) = 1.8 Hz, CH_2), 26.25 (d, ^1J(CP) = 64.6 Hz, PCH_2), 122.21 (d, ^3J(CP) = 5.4 Hz, *o*-OPh), 124.63 (s, *p*-OPh), 129.26 (d, ^3J(CP) = 12.6 Hz, *m*-Ph), 129.54 (s, *m*-OPh), 129.60 (dd, ^1J(CP) = 105.3 Hz, ^3J(CP) = 6.0 Hz, *i*-Ph), 131.77 (d, ^2J(CP) = 10.8 Hz, *o*-Ph), 132.77 (d, ^4J(CP) = 1.2 Hz, *p*-Ph), 152.61 (d, ^2J(CP) = 9.6 Hz, *i*-OPh).

***4a*.** Yield: 0.710 g, 90% (Found: C, 57.78; H, 6.75; N, 3.62. $C_{38}H_{52}O_4P_4N_2S_2$ requires C, 57.86; H, 6.64; N, 3.55%); ν_{max}/cm^{-1} (KBr) 483w, 519m, 533s, 620w, 696m, 722m, 750m, 786m, 822w, 846m, 945s, 1040vs, 1098w, 1117m, 1180w, 1209s, 1245s, 1387w, 1436s, 1482w, 2892w, 2934w, 2977m, 3053w; δ_H ($CDCl_3$) 1.14 (t, 12H, ^3J(HH) = 6.8 Hz, CH_3), 1.34 and 1.51 (m, 4H each, CH_2), 2.62 (m, 4H, PCH_2), 3.92 (m, 8H, OCH_2), 7.39–7.46 (m, 12H, Ph), 7.67–7.74 (m, 8H, Ph); δ_C ($CDCl_3$) 16.04 (d, ^3J(CP) = 8.1 Hz, CH_3), 21.32 (d, ^2J(CP) = 3.5 Hz, CH_2), 26.76 (d, ^1J(CP) = 65.8 Hz, PCH_2), 29.92 (d, ^3J(CP) = 15.7 Hz, CH_2), 61.73 (d, ^2J(CP) = 5.8 Hz, OCH_2), 128.58 (d, ^3J(CP) = 12.2 Hz, *m*-Ph), 129.91 (dd, ^1J(CP) = 104.2 Hz, ^3J(CP) = 5.8 Hz, *i*-Ph), 131.35 (d, ^2J(CP) = 10.5 Hz, *o*-Ph), 132.02 (s, *p*-Ph).

***4b*.** Yield: 0.922 g, 94% (Found: C, 65.89; H, 5.25; N, 2.99. $C_{54}H_{52}O_4P_4N_2S_2$ requires C, 66.11; H, 5.34; N, 2.85%); ν_{max}/cm^{-1} (KBr) 498w, 516w, 532m, 604w, 691m, 734m, 766m, 786s, 849m, 886s, 908s, 1024w, 1115w, 1161w, 1189m, 1199vs, 1289m, 1437m, 1487s, 1590m, 2863w, 2932w, 2942w, 3055w; δ_H ($CDCl_3$) 1.27 and 1.40 (m, 4H each, CH_2), 2.60 (m, 4H, PCH_2), 7.10–7.29 (m, 20H, Ph), 7.41–7.64 (m, 20H, Ph); δ_C ($CDCl_3$) 21.11 (s, CH_2), 26.44 (d, ^1J(CP) = 66.2 Hz, PCH_2), 29.74 (d, ^3J(CP) = 14.9 Hz, CH_2), 121.58 (d, ^3J(CP) = 4.8 Hz, *o*-OPh), 123.99 (s, *p*-OPh), 128.63 (d, ^3J(CP) = 12.6 Hz, *m*-Ph), 128.93 (s, *m*-OPh), 129.14 (dd, ^1J(CP) = 102.4 Hz, ^3J(CP) = 5.6 Hz, *i*-Ph), 131.28 (d, ^2J(CP) = 10.0 Hz, *o*-Ph), 132.12 (d, ^4J(CP) = 2.2 Hz, *p*-Ph), 152.03 (d, ^2J(CP) = 9.3 Hz, *i*-OPh).

$Fe(\eta^5\text{-}C_5H_4[P\{=NP(=S)(OR)_2\}Ph_2])_2$ (R = Et 5a, Ph 5b) and $Fe(\eta^5\text{-}C_5H_4[P\{=NP(=S)(OR)_2\}{}^iPr_2])_2$ (R = Et 6a, Ph 6b). Compounds **5–6a**,**b**, isolated as air-stable yellow solids, were prepared as described for **2–4a**,**b** starting from the corresponding ferrocenyl-diphosphine, *i.e.* dppf or dippf (1 mmol), and the appropriate azide $(RO)_2P(=S)N_3$ (R = Et, Ph; 2.2 mmol).

***5a*.** Yield: 0.799 g, 90% (Found: C, 56.62; H, 5.53; N, 3.26. $FeC_{42}H_{48}O_4P_4N_2S_2$ requires C, 56.76; H, 5.44; N, 3.15%); ν_{max}/cm^{-1} (KBr) 496m, 559m, 586w, 623w, 695m, 721m, 746m, 776s, 820m, 944s, 988w, 1026vs, 1114s, 1161w, 1177m, 1266s, 1301s, 1319m, 1364w, 1437m, 1483w, 1588w, 2891w, 2932w, 2976m, 3061w; δ_H ($CDCl_3$) 1.22 (t, 12H, ^3J(HH) = 7.1 Hz, CH_3), 4.00 (m, 8H, OCH_2), 4.47 and 4.80 (br, 4H each, C_5H_4), 7.28–7.39 (m, 8H, Ph), 7.42–7.64 (m, 12H, Ph); δ_C ($CDCl_3$) 16.01 (d, ^3J(CP) = 8.5 Hz, CH_3), 61.86 (d, ^2J(CP) = 6.3 Hz, OCH_2), 72.90 (dd, ^1J(CP) = 122.1 Hz, ^3J(CP) = 2.2 Hz, C of C_5H_4), 74.27 (d, ^3J(CP) = 13.8 Hz, CH of C_5H_4), 74.96 (d, ^2J(CP) = 10.8 Hz, CH of C_5H_4), 128.08 (d, ^3J(CP) = 13.0 Hz, *m*-Ph), 130.66 (dd, ^1J(CP) = 109.8 Hz, ^3J(CP) = 3.7 Hz, *i*-Ph), 131.96 (s, *p*-Ph), 132.00 (d, ^2J(CP) = 10.8 Hz, *o*-Ph).

5b. Yield: 0.919 g, 85% (Found: C, 64.37; H, 4.59; N, 2.70. $FeC_{58}H_{48}O_4P_4N_2S_2$ requires C, 64.45; H, 4.48; N, 2.59%); ν_{max}/cm^{-1} (KBr) 486w, 481m, 523w, 555m, 634w, 687s, 743s, 774s, 830m, 880s, 910s, 1026w, 1116m, 1192s, 1210vs, 1274s, 1436m, 1481s, 1593m, 2963w, 3021w, 3047w, 3068w; δ_H ($CDCl_3$) 4.34 and 4.60 (br, 4H each, C_5H_4), 7.12–7.34 (m, 20H, Ph), 7.41–7.58 (m, 20H, Ph); δ_C ($CDCl_3$) 72.40 (dd, ^1J(CP) = 122.5 Hz, ^3J(CP) = 3.3 Hz, C of C_5H_4), 74.44 (d, ^3J(CP) = 13.8 Hz, CH of C_5H_4), 75.41 (d, ^2J(CP) = 11.2 Hz, CH of C_5H_4), 121.69 (d, ^3J(CP) = 5.2 Hz, *o*-OPh), 124.43 (s, *p*-OPh), 128.58 (d, ^3J(CP) = 13.0 Hz, *m*-Ph), 129.47 (s, *m*-OPh), 130.14 (dd, ^1J(CP) = 108.7 Hz, ^3J(CP) = 3.7 Hz, *i*-Ph), 132.33 (d, ^2J(CP) = 11.2 Hz, *o*-Ph), 132.63 (d, ^4J(CP) = 2.6 Hz, *p*-Ph), 152.63 (d, ^2J(CP) = 9.3 Hz, *i*-OPh).

6a. Yield: 0.662 g, 88% (Found: C, 47.73; H, 7.44; N, 3.84. $FeC_{30}H_{56}O_4P_4N_2S_2$ requires C, 47.87; H, 7.50; N, 3.72%); ν_{max}/cm^{-1} (KBr) 488w, 501m, 578w, 632w, 660s, 684m, 753s, 813m, 887w, 943s, 1038vs, 1096m, 1175s, 1202w, 1246s, 1315s, 1391s, 1464m, 2893m, 2935m, 2973s, 3082w; δ_H ($CDCl_3$) 1.17–1.37 (m, 36H, CH_3 and $CH(CH_3)_2$), 2.49 (m, 4H, $CH(CH_3)_2$), 4.11 (m, 8H, OCH_2), 4.69 and 4.86 (br, 4H each, C_5H_4); δ_C ($CDCl_3$) 16.50 (m, CH_3 and $CH(CH_3)_2$), 26.15 (d, ^1J(CP) = 68.5 Hz, $CH(CH_3)_2$), 61.69 (d, ^2J(CP) = 6.3 Hz, OCH_2), 71.39 (dd, ^1J(CP) = 103.1 Hz, ^3J(CP) = 4.4 Hz, C of C_5H_4), 73.54 (d, ^3J(CP) = 11.2 Hz, CH of C_5H_4), 73.92 (d, ^2J(CP) = 9.7 Hz, CH of C_5H_4).

6b. Yield: 0.869 g, 92% (Found: C, 58.23; H, 6.03; N, 3.11. $FeC_{46}H_{56}O_4P_4N_2S_2$ requires C, 58.47; H, 5.97; N, 2.96%); ν_{max}/cm^{-1} (KBr) 500m, 567w, 599w, 659s, 689s, 729m, 772s, 812m, 887s, 910s, 1025w, 1043w, 1174m, 1200vs, 1251w, 1323s, 1391w, 1488s, 1591s, 2873w, 2934w, 2966m, 3073w; δ_H ($CDCl_3$) 1.17 (m, 24H, $CH(CH_3)_2$), 2.42 (m, 4H, $CH(CH_3)_2$), 4.55 and 4.70 (br, 4H each, C_5H_4), 7.15 (m, 4H, Ph), 7.33–7.42 (m, 16H, Ph); δ_C ($CDCl_3$) 16.22 (dd, ^2J(CP) = 46.6 Hz, ^4J(CP) = 1.9 Hz, $CH(CH_3)_2$), 25.79 (d, ^1J(CP) = 67.6 Hz, $CH(CH_3)_2$), 70.22 (dd, ^1J(CP) = 104.2 Hz, ^3J(CP) = 5.2 Hz, C of C_5H_4), 73.64 (d, ^3J(CP) = 11.1 Hz, CH of C_5H_4), 74.06 (d, ^2J(CP) = 9.5 Hz, CH of C_5H_4), 121.36 (d, ^3J(CP) = 5.2 Hz, *o*-OPh), 124.08 (s, *p*-OPh), 129.25 (s, *m*-OPh), 152.53 (d, ^2J(CP) = 9.3 Hz, *i*-OPh).

$[Ag\{\kappa^2(S,S')\text{-}(CH_2)_n[P\{=NP(=S)(OR)_2\}Ph_2]_2\}][SbF_6]$ (*n* = 1, R = Et 7a, Ph 7b; *n* = 2, R = Et 8a, Ph 8b). A solution of the corresponding bis(iminophosphorane) ligand **1–2a**,**b** (0.5 mmol) in 30 cm^3 of dichloromethane was treated, at room temperature and in the absence of light, with $AgSbF_6$ (0.172 g, 0.5 mmol) for 1 h. The solvent was then removed under reduced pressure to give a white solid which was washed with diethyl ether (3 × 20 cm^3) and dried *in vacuo*.

7a. Yield: 0.430 g, 81% (Found: C, 37.19; H, 3.87; N, 2.66. $AgC_{33}H_{42}F_6O_4P_4N_2S_2Sb$ requires C, 37.31; H, 3.98; N, 2.64%); conductivity (acetone, 20 °C) 128 Ω^{-1} cm^2 mol^{-1}; ν_{max}/cm^{-1} (KBr) 495m, 541w, 590m, 658vs (SbF_6^-), 690s, 721m, 744s, 847w, 961s, 1023vs, 1116s, 1173m, 1242vs, 1437s, 1483w, 1589w, 2899w, 2981m, 3060w; δ_H ($CDCl_3$) 1.10 (t, 12H, ^3J(HH) = 7.0 Hz, CH_3), 3.94 (m, 8H, OCH_2), 4.11 (t, 2H, ^2J(HP) = 13.4 Hz, PCH_2), 7.23–7.65 (m, 20H, Ph); δ_C ($CDCl_3$) 15.66 (d, ^3J(CP) = 8.7 Hz, CH_3), 22.73 (tt, ^1J(CP) = 71.2 Hz, ^3J(CP) = 5.7 Hz, PCH_2), 64.10 (d, ^2J(CP) = 7.0 Hz, OCH_2), 127.23 (dd, ^1J(CP) = 107.1 Hz, ^3J(CP) = 2.3 Hz, *i*-Ph), 129.06 (d, ^3J(CP) = 12.8 Hz, *m*-Ph), 131.60 (d, ^2J(CP) = 10.9 Hz, *o*-Ph), 133.24 (s, *p*-Ph); MS (FAB) *m*/*z* 827.9 (100%) [M^+ + 1].

7b. Yield: 0.520 g, 83% (Found: C, 46.79; H, 3.43; N, 2.12. $AgC_{49}H_{42}F_6O_4P_4N_2S_2Sb$ requires C, 46.91; H, 3.37; N, 2.23%); conductivity (acetone, 20 °C) 121 Ω^{-1} cm^2 mol^{-1}; ν_{max}/cm^{-1} (KBr) 500m, 600w, 618w, 658s (SbF_6^-), 689s, 744m, 771s, 834w, 927s, 1006w, 1024m, 1070w, 1165m, 1171s, 1193vs, 1280s, 1437m, 1487s, 1589m, 2895w, 2940w, 3060w; δ_H (CD_2Cl_2) 4.12 (t, 2H, ^2J(HP) = 13.7 Hz, PCH_2), 6.94–7.57 (m, 30H, Ph); δ_C (CD_2Cl_2) 27.84 (tt, ^1J(CP) = 68.7 Hz, ^3J(CP) = 5.5 Hz, PCH_2), 121.29 (d, ^3J(CP) = 4.8 Hz, *o*-OPh), 125.91 (s, *p*-OPh), 126.63 (dd, ^1J(CP) = 108.7 Hz, ^3J(CP) = 3.0 Hz, *i*-Ph), 129.56 (d, ^3J(CP) = 12.9 Hz, *m*-Ph), 130.19 (s, *m*-OPh), 132.24 (d, ^2J(CP) = 10.7 Hz, *o*-Ph), 134.04 (s, *p*-Ph), 151.46 (d, ^2J(CP) = 10.2 Hz, *i*-OPh); MS (FAB) *m*/*z* 1019.8 (30%) [M^+ + 1].

8a. Yield: 0.468 g, 87% (Found: C, 37.88; H, 4.16; N, 2.73. $AgC_{34}H_{44}F_6O_4P_4N_2S_2Sb$ requires C, 37.94; H, 4.12; N, 2.60%); conductivity (acetone, 20 °C) 119 Ω^{-1} cm^2 mol^{-1}; ν_{max}/cm^{-1} (KBr) 520m, 586w, 658s (SbF_6^-), 693s, 744s, 792m, 830w, 963s, 1026vs, 1120s, 1161w, 1182m, 1261s, 1301s, 1367w, 1390w, 1439m, 1590w, 2903w, 2936w, 2983m, 3060w; δ_H ($CDCl_3$) 1.23 (t, 12H, ^3J(HH) = 7.1 Hz, CH_3), 2.81 (br, 4H, PCH_2), 4.04 (m, 8H, OCH_2), 7.28–7.67 (m, 20H, Ph); δ_C ($CDCl_3$) 15.81 (d, ^3J(CP) = 8.6 Hz, CH_3), 20.65 (m, PCH_2), 64.26 (d, ^2J(CP) = 7.8 Hz, OCH_2), 126.10 (dd, ^1J(CP) = 105.3 Hz, ^3J(CP) = 4.8 Hz, *i*-Ph), 129.45 (d, ^3J(CP) = 12.9 Hz, *m*-Ph), 131.26 (d, ^2J(CP) = 10.7 Hz, *o*-Ph), 133.67 (s, *p*-Ph); MS (FAB) *m*/*z* 841.9 (100%) [M^+ + 1].

8b. Yield: 0.539 g, 85% (Found: C, 47.19; H, 3.41; N, 2.33. $AgC_{50}H_{44}F_6O_4P_4N_2S_2Sb$ requires C, 47.34; H, 3.50; N, 2.21%); conductivity (acetone, 20 °C) 113 Ω^{-1} cm^2 mol^{-1}; ν_{max}/cm^{-1} (KBr) 497w, 521m, 591w, 656s (SbF_6^-), 690s, 742m, 772s, 812w, 902m, 928s, 1023w, 1117m, 1160s, 1191vs, 1267m, 1296m, 1438w, 1486s, 1588m, 2905w, 2960w, 3059w; δ_H (CD_2Cl_2) 2.47 (br, 4H, PCH_2), 7.06–7.82 (m, 40H, Ph); δ_C (CD_2Cl_2) 19.35 (m, PCH_2), 121.63 (d, ^3J(CP) = 4.8 Hz, *o*-OPh), 125.14 (dd, ^1J(CP) = 104.7 Hz, ^3J(CP) = 5.4 Hz, *i*-Ph), 126.50 (s, *p*-OPh), 129.82 (d, ^3J(CP) = 13.0 Hz, *m*-Ph), 130.41 (s, *m*-OPh), 131.86 (d, ^2J(CP) = 10.9 Hz, *o*-Ph), 134.55 (s, *p*-Ph), 150.72 (d, ^2J(CP) = 9.6 Hz, *i*-OPh); MS (FAB) *m*/*z* 1033.8 (100%) [M^+ + 1].

$[Ag\{(CH_2)_n[P\{=NP(=S)(OR)_2\}Ph_2]_2\}]_x[SbF_6]_x$ (*n* = 4, R = Et 9a, Ph 9b; *n* = 6, R = Et 10a, Ph 10b). The polymeric compounds **9–10a**,**b**, isolated as air-stable white solids, were prepared as described for **7–8a**,**b** starting from the corresponding bis(iminophosphorane) ligand **3–4a**,**b** (0.5 mmol) and $AgSbF_6$ (0.172 g, 0.5 mmol).

9a. Yield: 0.442 g, 80% (Found: C, 39.22; H, 4.25; N, 2.60. $AgC_{36}H_{48}F_6O_4P_4N_2S_2Sb$ requires C, 39.15; H, 4.38; N, 2.54%); conductivity (acetone, 20 °C) 115 Ω^{-1} cm^2 mol^{-1}; ν_{max}/cm^{-1} (KBr) 513w, 542m, 576w, 660s (SbF_6^-), 694m, 722s, 750m, 791w, 827m, 962s, 1024vs, 1118s, 1161w, 1182m, 1264vs, 1366w, 1390w, 1438s, 1485m, 1590w, 2902w, 2941w, 2986m, 3058w; δ_H ($CDCl_3$) 1.19 (t, 12H, ^{3}J(HH) = 7.1 Hz, CH$_3$), 1.84 (m, 4H, CH$_2$), 2.80 (m, 4H, PCH$_2$), 3.98 (m, 8H, OCH$_2$), 7.50–7.59 (m, 12H, Ph), 7.68–7.75 (m, 8H, Ph); δ_C (CDCl$_3$) 15.87 (d, ^{3}J(CP) = 8.7 Hz, CH$_3$), 23.04 (dd, ^{3}J(CP) = 16.3 Hz, ^{2}J(CP) = 2.9 Hz, CH$_2$), 25.85 (d, ^{1}J(CP) = 65.8 Hz, PCH$_2$), 63.93 (d, ^{2}J(CP) = 7.6 Hz, OCH$_2$), 127.65 (dd, ^{1}J(CP) = 104.2 Hz, ^{3}J(CP) = 6.4 Hz, *i*-Ph), 129.19 (d, ^{3}J(CP) = 12.8 Hz, *m*-Ph), 131.17 (d, ^{2}J(CP) = 11.1 Hz, *o*-Ph), 132.96 (d, ^{4}J(CP) = 2.3 Hz, *p*-Ph); MS (FAB) *m*/*z* 869.7 (20%) [M$^+$ + 1].

9b. Yield: 0.570 g, 88% (Found: C, 48.02; H, 3.64; N, 2.30. AgC$_{52}$H$_{48}$F$_6$O$_4$P$_4$N$_2$S$_2$Sb requires C, 48.17; H, 3.73; N, 2.16%); conductivity (acetone, 20 °C) 109 Ω^{-1} cm^2 mol^{-1}; ν_{max}/cm^{-1} (KBr) 498w, 541m, 590w, 656s (SbF$_6^-$), 690s, 724w, 770s, 823m, 900s, 924s, 998w, 1023m, 1069w, 1118s, 1159s, 1188vs, 1301s, 1437s, 1454m, 1486s, 1588s, 2869w, 2931w, 3059w; δ_H (CD$_2$Cl$_2$) 1.69 (m, 4H, CH$_2$), 2.74 (m, 4H, PCH$_2$), 7.15–7.43 (m, 20H, Ph), 7.63–7.72 (m, 20H, Ph); δ_C (CD$_2$Cl$_2$) 23.27 (dd, ^{3}J(CP) = 19.7 Hz, ^{2}J(CP) = 3.0 Hz, CH$_2$), 25.38 (d, ^{1}J(CP) = 64.6 Hz, PCH$_2$), 121.21 (d, ^{3}J(CP) = 4.8 Hz, *o*-OPh), 126.15 (s, *p*-OPh), 127.09 (dd, ^{1}J(CP) = 105.3 Hz, ^{3}J(CP) = 6.1 Hz, *i*-Ph), 129.57 (d, ^{3}J(CP) = 13.2 Hz, *m*-Ph), 130.36 (s, *m*-OPh), 131.39 (d, ^{2}J(CP) = 11.4 Hz, *o*-Ph), 133.60 (s, *p*-Ph), 150.89 (d, ^{2}J(CP) = 9.6 Hz, *i*-OPh); MS (FAB) *m*/*z* 1061.8 (100%) [M$^+$ + 1].

10a. Yield: 0.436 g, 77% (Found: C, 40.21; H, 4.75; N, 2.53. AgC$_{38}$H$_{52}$F$_6$O$_4$P$_4$N$_2$S$_2$Sb requires C, 40.30; H, 4.63; N, 2.47%); conductivity (acetone, 20 °C) 114 Ω^{-1} cm^2 mol^{-1}; ν_{max}/cm^{-1} (KBr) 511w, 533m, 583w, 657s (SbF$_6^-$), 693s, 721m, 745m, 792w, 838w, 961s, 1025vs, 1117s, 1160w, 1186w, 1263s, 1367w, 1389w, 1438m, 2865w, 2901w, 2934w, 2982w, 3058w; δ_H (CD$_2$Cl$_2$) 1.16 (t, 12H, ^{3}J(HH) = 6.8 Hz, CH$_3$), 1.50 and 1.64 (m, 4H each, CH$_2$), 2.56 (m, 4H, PCH$_2$), 3.97 (m, 8H, OCH$_2$), 7.51–7.73 (m, 20H, Ph); δ_C (CD$_2$Cl$_2$) 16.14 (d, ^{3}J(CP) = 8.2 Hz, CH$_3$), 21.36 (d, ^{2}J(CP) = 4.1 Hz, CH$_2$), 27.81 (d, ^{1}J(CP) = 67.0 Hz, PCH$_2$), 29.85 (d, ^{3}J(CP) = 15.7 Hz, CH$_2$), 64.54 (d, ^{2}J(CP) = 7.6 Hz, OCH$_2$), 128.51 (dd, ^{1}J(CP) = 103.1 Hz, ^{3}J(CP) = 5.2 Hz, *i*-Ph), 129.60 (d, ^{3}J(CP) = 12.8 Hz, *m*-Ph), 131.67 (d, ^{2}J(CP) = 11.1 Hz, *o*-Ph), 133.48 (d, ^{4}J(CP) = 2.3 Hz, *p*-Ph); MS (FAB) *m*/*z* 897.7 (30%) [M$^+$ + 1].

10b. Yield: 0.556 g, 84% (Found: C, 48.85; H, 3.99; N, 2.28. AgC$_{54}$H$_{52}$F$_6$O$_4$P$_4$N$_2$S$_2$Sb requires C, 48.96; H, 3.96; N, 2.11%); conductivity (acetone, 20 °C) 108 Ω^{-1} cm^2 mol^{-1}; ν_{max}/cm^{-1} (KBr) 499w, 531m, 590w, 657s (SbF$_6^-$), 690s, 744m, 769s, 888w, 900s, 922s, 998w, 1023w, 1069w, 1117s, 1159s, 1187vs, 1303s, 1437m, 1486s, 1589s, 2863w, 2932w, 3059w; δ_H (CDCl$_3$) 1.43 (m, 8H, CH$_2$), 2.61 (m, 4H, PCH$_2$), 7.05–7.30 (m, 20H, Ph), 7.46–7.65 (m, 20H, Ph); δ_C (CDCl$_3$) 21.07 (d, ^{2}J(CP) = 3.3 Hz, CH$_2$), 26.49 (d, ^{1}J(CP) = 67.4 Hz, PCH$_2$), 29.25 (d, ^{3}J(CP) = 16.0 Hz, CH$_2$), 120.86 (d, ^{3}J(CP) = 4.8 Hz, *o*-OPh), 125.68 (s, *p*-OPh), 127.27 (dd, ^{1}J(CP) = 104.2 Hz, ^{3}J(CP) = 5.2 Hz, *i*-Ph), 129.13 (d, ^{3}J(CP) = 13.0 Hz, *m*-Ph), 129.93 (s, *m*-OPh), 131.12 (d, ^{2}J(CP) = 10.8 Hz, *o*-Ph), 132.92 (d, ^{4}J(CP) = 1.9 Hz, *p*-Ph), 150.68 (d, ^{2}J(CP) = 10.1 Hz, *i*-OPh); MS (FAB) *m*/*z* 1089.9 (100%) [M$^+$ + 1].

[Ag{Fe(η^5-C$_5$H$_4$[P{=NP(=S)(OR)$_2$}Ph$_2$])$_2$}]$_x$[SbF$_6$]$_x$ (R = Et 11a, Ph 11b) and [Ag{Fe(η^5-C$_5$H$_4$[P{=NP(=S)(OR)$_2$}^{i}Pr$_2$])$_2$}]$_x$-[SbF$_6$]$_x$ (R = Et 12a, Ph 12b). The polymeric compounds **11–12a**,**b**, isolated as air-stable yellow-orange solids, were prepared as described for **7–8a**,**b** starting from the corresponding bis(iminophosphorane) ligand **5–6a**,**b** (0.5 mmol) and AgSbF$_6$ (0.172 g, 0.5 mmol).

11a. Yield: 0.487 g, 79% (Found: C, 41.11; H, 3.87; N, 2.33. AgFeC$_{42}$H$_{48}$F$_6$O$_4$P$_4$N$_2$S$_2$Sb requires C, 40.94; H, 3.92; N, 2.27%); conductivity (acetone, 20 °C) 116 Ω^{-1} cm^2 mol^{-1}; ν_{max}/cm^{-1} (KBr) 490w, 558w, 658s (SbF$_6^-$), 693m, 724w, 751m, 793w, 820w, 961m, 1026vs, 1116m, 1186w, 1262s, 1365w, 1389w, 1437w, 2900w, 2935w, 2981w, 3058w; δ_H (CDCl$_3$) 1.12 (t, 12H, ^{3}J(HH) = 7.0 Hz, CH$_3$), 3.94 (m, 8H, OCH$_2$), 4.30 and 4.50 (br, 4H each, C$_5$H$_4$), 7.30–7.67 (m, 20H, Ph); δ_C (CDCl$_3$) 15.69 (d, ^{3}J(CP) = 8.2 Hz, CH$_3$), 64.10 (d, ^{2}J(CP) = 7.0 Hz, OCH$_2$), 71.95 (dd, ^{1}J(CP) = 124.0 Hz, ^{3}J(CP) = 4.1 Hz, C of C$_5$H$_4$), 74.38 (d, ^{2}J(CP) = 8.2 Hz, CH of C$_5$H$_4$), 74.54 (d, ^{3}J(CP) = 11.0 Hz, CH of C$_5$H$_4$), 128.82 (d, ^{3}J(CP) = 12.8 Hz, *m*-Ph), 129.33 (dd, ^{1}J(CP) = 106.0 Hz, ^{3}J(CP) = 4.7 Hz, *i*-Ph), 132.04 (d, ^{2}J(CP) = 11.6 Hz, *o*-Ph), 133.23 (s, *p*-Ph); MS (FAB) *m*/*z* 997.7 (100%) [M$^+$ + 1].

11b. Yield: 0.598 g, 84% (Found: C, 49.04; H, 3.37; N, 2.09. AgFeC$_{58}$H$_{48}$F$_6$O$_4$P$_4$N$_2$S$_2$Sb requires C, 48.90; H, 3.40; N, 1.97%); conductivity (acetone, 20 °C) 113 Ω^{-1} cm^2 mol^{-1}; ν_{max}/cm^{-1} (KBr) 492w, 562w, 595w, 657s (SbF$_6^-$), 690s, 727m, 768m, 811w, 901m, 924s, 1024w, 1117w, 1160m, 1187vs, 1294s, 1437w, 1486m, 1589w, 2924w, 2964w, 3023w, 3059w; δ_H (CD$_2$Cl$_2$) 4.42 and 4.60 (br, 4H each, C$_5$H$_4$), 7.04–7.39 (m, 20H, Ph), 7.50–7.75 (m, 20H, Ph); δ_C (CD$_2$Cl$_2$) 71.69 (dd, ^{1}J(CP) = 123.3 Hz, ^{3}J(CP) = 3.0 Hz, C of C$_5$H$_4$), 74.60 (d, ^{3}J(CP) = 13.8 Hz, CH of C$_5$H$_4$), 75.25 (d, ^{2}J(CP) = 10.7 Hz, CH of C$_5$H$_4$), 121.19 (d, ^{3}J(CP) = 4.8 Hz, *o*-OPh), 126.25 (s, *p*-OPh), 128.20 (dd, ^{1}J(CP) = 108.3 Hz, ^{3}J(CP) = 3.6 Hz, *i*-Ph), 129.28 (d, ^{3}J(CP) = 13.8 Hz, *m*-Ph), 130.44 (s, *m*-OPh), 132.31 (d, ^{2}J(CP) = 11.4 Hz, *o*-Ph), 133.86 (d, ^{4}J(CP) = 1.8 Hz, *p*-Ph), 151.16 (d, ^{2}J(CP) = 10.8 Hz, *i*-OPh); MS (FAB) *m*/*z* 1189.2 (50%) [M$^+$ + 1].

12a. Yield: 0.449 g, 82% (Found: C, 32.79; H, 5.30; N, 2.67. AgFeC$_{30}$H$_{56}$F$_6$O$_4$P$_4$N$_2$S$_2$Sb requires C, 32.87; H, 5.15; N, 2.56%); conductivity (acetone, 20 °C) 115 Ω^{-1} cm^2 mol^{-1}; ν_{max}/cm^{-1} (KBr) 482w, 503w, 567m, 657vs (SbF$_6^-$), 689w, 745m, 788w, 816w, 884w, 959s, 1028vs, 1098w, 1175m, 1246s, 1303s, 1368m, 1395m, 1466w, 2875w, 2901w, 2937m, 2979m, 3114w; δ_H (CDCl$_3$) 1.24–1.44 (m, 36H, CH$_3$ and CH(C*H*$_3$)$_2$), 2.45 (m, 4H, C*H*(CH$_3$)$_2$), 4.20 (m, 8H, OCH$_2$), 4.84 and 4.89 (br, 4H each, C$_5$H$_4$); δ_C (CDCl$_3$) 15.97 (m, CH$_3$ and CH(*C*H$_3$)$_2$), 26.70 (d, ^{1}J(CP) = 65.9 Hz, *C*H(CH$_3$)$_2$), 64.09 (d, ^{2}J(CP) = 7.8 Hz, OCH$_2$), 70.21 (dd, ^{1}J(CP) = 107.2 Hz, ^{3}J(CP) = 5.9 Hz, C of C$_5$H$_4$), 73.60 (d, ^{3}J(CP) = 11.9 Hz, CH of C$_5$H$_4$), 74.24 (d, ^{2}J(CP) = 10.0 Hz, CH of C$_5$H$_4$); MS (FAB) *m*/*z* 861.5 (100%) [M$^+$ + 1].

Yield: 0.554 g, 86% (Found: C, 42.76; H, 4.44; N, 2.30. AgFeC$_{46}$H$_{56}$F$_6$O$_4$P$_4$N$_2$S$_2$Sb requires C, 42.88; H, 4.38; N, 2.17%); conductivity (acetone, 20 °C) 108 Ω^{-1} cm^2 mol^{-1}; ν_{max}/cm^{-1} (KBr) 499m, 552w, 587m, 656s (SbF$_6^-$), 690s, 728w, 765s, 805w, 839w, 898m, 920s, 1005w, 1023w, 1043w, 1160s, 1189vs, 1325s, 1395m, 1462w, 1487s, 1589s, 2874w, 2935w, 2970w, 3066w; δ_H (CD$_2$Cl$_2$) 1.22 (m, 24H, CH(C*H*$_3$)$_2$), 2.44 (m, 4H, C*H*(CH$_3$)$_2$), 4.62 and 4.72 (br, 4H each, C$_5$H$_4$), 7.27–7.31 (m, 12H, Ph), 7.40–7.45 (m, 8H, Ph); δ_C (CD$_2$Cl$_2$) 16.42 (dd, ^{2}J(CP) = 49.1 Hz, ^{4}J(CP) = 1.8 Hz, CH(*C*H$_3$)$_2$), 26.71 (d, ^{1}J(CP) = 65.8 Hz, *C*H(CH$_3$)$_2$), 69.60 (dd, ^{1}J(CP) = 101.7 Hz, ^{3}J(CP) = 6.0 Hz, C of C$_5$H$_4$), 73.92 (d, ^{3}J(CP) = 12.0 Hz, CH of C$_5$H$_4$), 74.72 (d, ^{2}J(CP) = 10.2 Hz, CH of C$_5$H$_4$), 121.40 (d, ^{3}J(CP) = 4.8 Hz, *o*-OPh), 126.21 (s, *p*-OPh), 130.59 (s, *m*-OPh), 151.67 (d, ^{2}J(CP) = 10.2 Hz, *i*-OPh); MS (FAB) *m*/*z* 1053.8 (100%) [M$^+$ + 1].

Table 2 Crystal data and structure refinement for compounds **1b**, **7a**, **8b**, **9a** and **11b**

	1b	**7a**	**8b**	**9a**	**11b**
Empirical formula	$C_{49}H_{42}O_4P_4N_2S_2$	$Ag_2C_{66}H_{84}F_{12}O_8P_8N_4S_4Sb_2$	$2(AgC_{50}H_{44}F_6O_4P_4N_2S_2Sb)\cdot CH_2Cl_2$	$AgC_{36}H_{48}F_6O_4P_4N_2S_2Sb$	$AgFeC_{58}H_{48}F_6O_4P_4N_2S_2Sb\cdot 2CH_2Cl_2$
Formula weight	910.85	2124.61	2621.91	1104.38	1594.31
Temperature/K	293(2)	200(2)	150(2)	293(2)	150(2)
Wavelength/Å	1.54180	1.54180	1.54180	1.54180	1.54180
Crystal system	Monoclinic	Triclinic	Monoclinic	Triclinic	Monoclinic
Space group	$C2/c$	$P\bar{1}$	$P2/c$	$P\bar{1}$	$P2_1/c$
a/Å	29.2141(9)	11.1280(11)	25.8436(10)	12.1650(2)	17.9823(3)
b/Å	9.1678(2)	11.3219(9)	10.8312(5)	12.5716(2)	15.1788(3)
c/Å	20.1846(6)	18.1350(2)	20.3081(10)	16.4500(4)	24.4432(6)
α/°	90	87.206(6)	90	80.715(1)	90
β/°	123.056(2)	77.029(9)	109.556(5)	80.171(1)	102.802(1)
γ/°	90	70.753(7)	90	68.973(1)	90
Z	4	1	2	2	4
Volume/Å^3	4531.0(2)	2101.3(3)	5356.6(4)	2300.02(8)	6505.9(2)
Calculated density/g cm^{-3}	1.335	1.679	1.626	1.595	1.628
μ/mm^{-1}	2.777	11.774	9.821	10.781	11.011
F(000)	1896	1060	2620	1108	3184
Crystal size/mm	0.10 × 0.05 × 0.025	0.175 × 0.05 × 0.025	0.30 × 0.19 × 0.17	0.40 × 0.25 × 0.20	0.25 × 0.10 × 0.07
θ range/°	3.61 to 69.52	2.50 to 58.97	4.08 to 68.43	2.74 to 68.51	2.52 to 68.53
No. of reflns. collected	17433	40313	90615	46637	74429
No. of unique reflns.	4120 [R(int) = 0.067]	6029 [R(int) = 0.048]	9770 [R(int) = 0.0472]	8383 [R(int) = 0.0751]	11918 [R(int) = 0.0965]
Completeness to θ_{max}	96.6%	99.7%	99.1%	98.9%	99.3%
No. of parameters/restraints	360/0	478/0	634/2	506/0	768/1
Goodness-of-fit on F^2	0.896	1.156	1.045	1.058	1.069
Weight function (a, b)	0.0386, 0	0.0706, 4.6127	0.0696, 15.4293	0.1663, 3.1771	0.1231, 22.3918
R_1 [$I > 2\sigma(I)$][a]	0.0436	0.0389	0.0458	0.0825	0.0743
wR_2 [$I > 2\sigma(I)$][a]	0.1030	0.1034	0.1206	0.2396	0.2007
R_1 (all data)	0.0697	0.0495	0.0497	0.0913	0.0971
wR_2 (all data)	0.1139	0.1582	0.1268	0.2505	0.2171
Largest diff. peak and hole/e Å^{-3}	0.324 and −0.429	1.157 and −0.825	2.316 and −1.421	3.059 and −2.110	3.238 and −2.437

[a] $R_1 = \sum(|F_o| - |F_c|)/\sum|F_o|$; $wR_2 = \{\sum[w(F_o^2 - F_c^2)^2]/\sum[w(F_o^2)^2]\}^{1/2}$.

X-Ray crystal structure determination of compounds 1b, 7a, 8b, 9a and 11b

Crystals suitable for X-ray diffraction analysis were obtained by slow diffusion of *n*-hexane (**1b** and **7a**) or *n*-pentane (**8b**, **9a** and **11b**) into a saturated solution of the corresponding complex in dichloromethane. The most relevant crystal and refinement data are collected in Table 2. Diffraction data were recorded on a Nonius Kappa CCD single-crystal diffractometer, using Cu-Kα radiation ($\lambda = 1.5418$ Å). The data were collected using the oscillation method, with 2° oscillation and 40 s exposure time per frame, and with a crystal-to-detector distance of 29 mm. The data-collection strategy was calculated with the program Collect.[18] Data reduction and cell refinement were performed using the programs HKL Denzo and Scalepack.[19] Absorption correction was applied by means of SORTAV.[20]

The software package WINGX was used in all cases for space group determination, structure solution and refinement.[21] The structures were solved by Patterson interpretation and phase expansion using DIRDIF.[22] Isotropic least-squares refinement on F^2 using SHELXL97 was performed.[23] During the final stages of the refinements, all non-hydrogen atoms were refined with anisotropic displacement parameters (except the F(6a) and F(6b) atoms of the SbF_6^- anion in **11b**; this highly disordered group was found and isotropically refined). In the crystal of **8b** one dichloromethane molecule of solvation per two formula units of the complex was found to be disordered over two positions related by the crystallographic symmetry operation ($1 - x, y, 1/2 - z$), with 0.5 site occupancy factors. Bond distances between C and Cl atoms in this dichlorometane molecule were restrained to a target value of 1.6(0.02) Å. The H atoms were geometrically located and their coordinates refined riding on their parent atoms (except in **1b** where the coordinates of the H atoms were found from difference Fourier maps and included in the refinement with isotropic parameters). In all cases, the maximum residual electron density is located near to heavier atoms, except for **8b** in which the highest residual peaks are close to the disordered solvent molecule. The function minimized was $[\sum wF_o^2 - F_c^2)/\sum w(F_o^2)]^{1/2}$ where $w = 1/[\sigma^2(F_o^2) + (aP)^2 + bP]$ (a and b values are collected in Table 2) with $\sigma^2(F_o^2)$ from counting statistics and $P = (\mathrm{Max}\,(F_o^2 + 2F_c^2)/3$. Atomic scattering factors were taken from the International Tables for X-ray Crystallography.[24] Geometrical calculations were made with PARST.[25] The crystallographic plots were made with PLATON.[26]

Acknowledgements

This work was supported by the Ministerio de Educación y Ciencia (MEC) of Spain (Project CTQ2006–08485/BQU) and the Gobierno del Principado de Asturias (FICYT Project IB05–035). V.C. thanks MEC and the European Social Fund for the award of a "Ramón y Cajal" contract.

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