Gold and Silver Complexes with the Ligands *N*-[Bis(isopropoxy)thiophosphoryl]thiobenzamide and *N*-[Bis(isopropoxy)thiophosphoryl]-*N′*-phenylthiourea

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Gold and silver complexes with the *N*-[bis(isopropoxy)thiophosphoryl]thiobenzamide (HL^1) and *N*-[bis(isopropoxy)thiophosphoryl]-*N′*-phenylthiourea (HL^2) ligands are reported. The compounds [M(HL)(PPh$_3$)]TfO, [Ag(HL)(TfO)] and [Ag(HL)(PPh$_3$)$_2$]TfO were obtained by the reaction of both ligands with the corresponding trifluoromethanesulfonate salts. The (acetylacetonato)gold and -silver materials [M(acac)(PPh$_3$)] or [Au(acac)(C$_6$F$_5$)$_2$] cause deprotonation of the ligands and afford [ML(PPh$_3$)] or [AuL(C$_6$F$_5$)$_2$], whereas the reaction of [Au(TfO)(PPh$_3$)] with HL^1 in a 2:1 molar ratio in KOH/MeOH affords [Au$_2$(L^1)(PPh$_3$)$_2$]TfO. The first homoleptic anionic metal compounds [Au^{I}L$_2$]$^-$ are also reported.

Introduction

The chemistry of chelating ligands attached to metal centers through sulfur atoms has been extensively investigated. Unusual coordination at the metal centers and interesting stereochemistries of the chelate rings have been found. Among them, the coordination chemistry of *N*-(thiophosphoryl)thioamides or *N*-(thiophosphoryl)thioureas has been studied and extraction of metals using *N*-[bis(isopropoxy)thiophosphoryl]thiobenzamide has been reported[1] as well as a liquid ion-selective electrode for Hg^{2+} determination.[2] Different R^{1}C(X)NHP(Y)R^{2}R^3 ligands have been reported[3−10] (R^1 = R-NH or NX$_2$ X = H, alkyl or aryl group; R^2, R^3 = alkyl, aryl, alkoxy or aryloxy group, X = O, S; Y = O, S, Se) and despite the tautomeric forms in which they can exist, infrared studies on some of them support the presence of structures in which two double bonds C=S and P=S are present[7] although delocalization of the C−NH−P unit has been found as more representative of the bonding in the crystal structures[11] of PhC(S)NHP(S)(OR)$_2$ (R = *i*Pr, Et). The species consisting on one 1,10-diaza-18-crown-6 with two "(O*i*Pr)$_2$P(S)NHC(S)" units bonded to the nitrogen atoms has also been described.[8]

A brief overview of the chemistry with representative elements includes the potassium derivatives in which the metal atom is bonded to the sulfur atoms of "(O*i*Pr)$_2$P(S)NHC(S)Ph". The potassium atom can be in the center of a diaza-18-crown-6 cycle, or as part of a more complicated structure.[12,13] Other examples of coordination to representative elements include the mononuclear hexacoordinate compounds prepared from the reactions of different ligands with SnCl$_4$ although the geometries were not confirmed by X-ray studies,[14] and the lead derivatives [Pb{(O*i*Pr)$_2$P(X)NC(S)Ph}$_2$].[15] The [M^{2+}L$_2$] stoichiometry is the most common among the transition metal complexes described so far (M = Ni, Co, Pt, Pd, Zn, Cd)[6,7,16−22] which have been confirmed in many cases by single-crystal X-ray diffraction studies.

Among the reported complexes, those containing the coinage metals are however scarcely represented. The synthesis of [Cu{PhNHC(S)NP(S)(O*i*Pr)$_2$}][5] and also the reduction of Cu^{II} to Cu^{I} with other ligands[23] such us PhNHC(S)NHP(S)Ph$_2$, Me$_2$NC(S)NHP(S)Ph$_2$, or Et$_2$NC(S)NHP(S)(OPh)$_2$ have been described. For the latter, the crystal structure[24] consists on a trinuclear derivative of formula [Cu{Et$_2$NC(S)NP(S)(OPh)$_2$}]$_3$. The three-coordinate environment of the copper atom in [Cu{PhC(O)NP(S)Ph$_2$}(PPh$_3$)][7] has also been described. To the best of our knowledge the only such silver complex reported is the tetranuclear derivative [Ag{PhC(S)NP(S)(O*i*Pr)$_2$}]$_4$,[25] but no related gold complexes have been described. In this paper we report the synthesis and characterization of gold and silver complexes with the *N*-[bis(isopropoxy)thiophosphoryl]thiobenzamide

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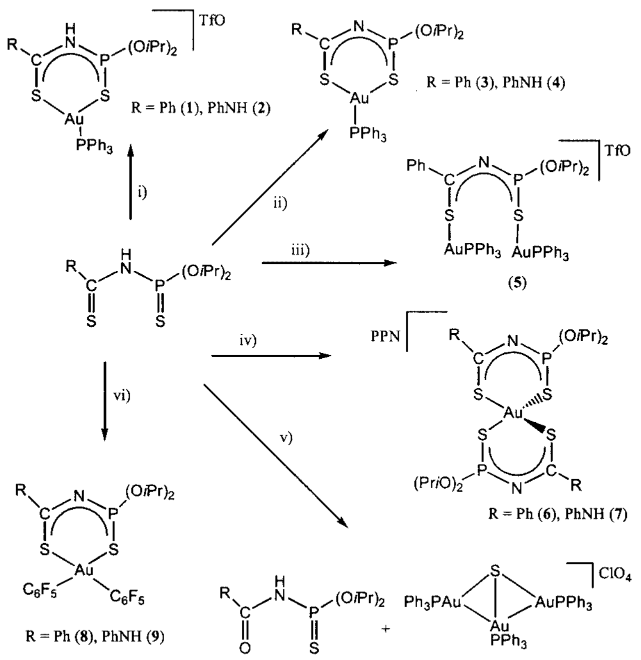
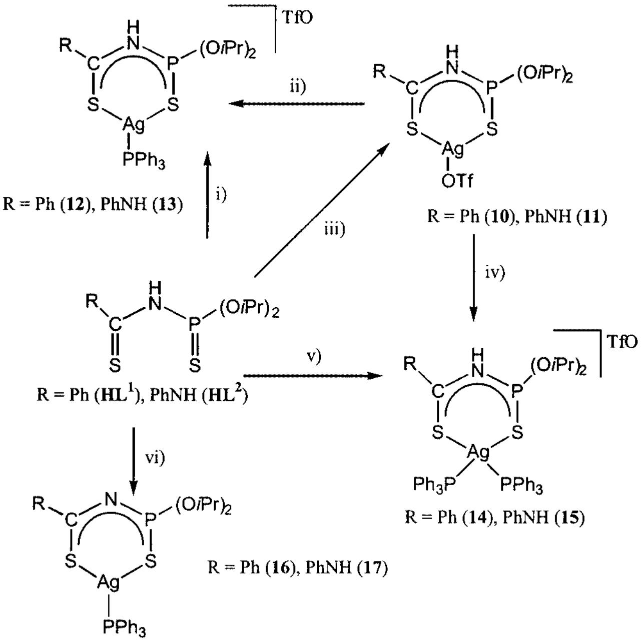
[PhC(S)NHP(S)(O*i*Pr)$_2$, HL^1) and *N*-[bis(isopropoxy)-thiophosphoryl]-*N'*-phenylthiourea (PhNHC(S)NHP(S)-(O*i*Pr)$_2$, HL^2) ligands (see Schemes 1 and 2). The first homoleptic anionic metal compounds [Au^{I}L$_2$]$^-$ are also reported. The previously reported derivatives are neutral (the metal oxidation state is +II) and different stoichiometries were obtained when the oxidation state was +I. In many of the derivatives shown here, coordination of the ligand takes place without any previous deprotonation of the ligands.



Scheme 1. i) [Au(TfO)(PPh$_3$)]/CH$_2$Cl$_2$, ii) [Au(TfO)(PPh$_3$)]/KOH, MeOH, iii) 2 [Au(TfO)(PPh$_3$)]/KOH, MeOH, iv) 1/2 PPN[Au(acac)$_2$]/CH$_2$Cl$_2$, 1/2 PPN[AuCl$_2$]/KOH, MeOH, v) [O{Au(PPh$_3$)}$_3$]ClO$_4$/CH$_2$Cl$_2$, vi) [Au(C$_6$F$_5$)$_2$(acac)]/CH$_2$Cl$_2$, NBu$_4$[Au(C$_6$F$_5$)$_2$]/KOH, MeOH



Scheme 2. i) [Ag(TfO)(PPh$_3$)]/CH$_2$Cl$_2$, ii) PPh$_3$, iii) AgTfO/CH$_2$Cl$_2$, iv) 2 PPh$_3$, v) [Ag(TfO)(PPh$_3$)$_2$]/CH$_2$Cl$_2$, vi) [Ag(TfO)(PPh$_3$)]/KOH, MeOH, [Ag(acac)(PPh$_3$)]/CH$_2$Cl$_2$

Results and Discussion

All the complexes described below are air and moisture stable. The behavior of their acetone solutions corresponds to their proposed neutral or ionic structures (Tables 1 and 2 show the conductivity values, yields, elemental analyses for C, H, N and S, NMR and mass spectral data for all the complexes presented). Characteristic absorptions are present in the IR spectra of the ligands.

Thus, in HL^1 the ν(NH) vibration appears at 3240 cm^{-1} and the ν(P=S) at 648. In HL^2 the ν(P=S) vibration appears at 640 cm^{-1}. Two ν(NH) vibrations appear at 3200 (Ph−NH) and 3063 cm^{-1} (C−NH−P), the second being observed as a shoulder of the nujol band in the spectrum of HL^2. In the discussion we will comment on the modification of the first band and the other band always appears as a shoulder on the nujol band in the complexes in which the ligand HL^2 has not been deprotonated. The shifts of the ν(P=S) IR band and the ^{31}P{^{1}H} NMR resonance due to the phosphorus atom of the ligand from those in the free ligands point to the involvement of the sulfur atom of the PS unit in the formation of the complexes. The shift of the ν(NH) vibration in the SCN(H)PS unit in the complexes which contain ligands which have not been deprotonated could point to the formation of a six-membered chelating ring. This is a reasonable proposal since tendency of the ligands to coordinate in a chelating form has already been shown in the literature and has also been confirmed by the X-ray structures of two of the compounds described herein.

Gold Complexes

The displacement of the labile trifluoromethanesulfonate ligand in [Au(TfO)(PPh$_3$)] affords the complexes [Au(HL^1)(PPh$_3$)]TfO (**1**) and [Au(HL^2)(PPh$_3$)]TfO (**2**). The vibrations corresponding to the anionic TfO groups are present in their IR spectra [ν_{asym}(SO$_3$) 1270, ν_{sym}(CF$_3$) 1225, ν_{asym}(CF$_3$) 1151, ν_{sym}(SO$_3$) 1033 cm^{-1}].[26] In **1** the ν(NH) absorption appears at 3242 cm^{-1} and the ν(P=S) at 579. In **2** they appear at 3205 and 580 cm^{-1}, respectively. In their ^{1}H NMR spectra the isopropyl hydrogen atoms appear at approximately $\delta = 1.3$ (CH$_3$) and 5.0 (CH) ppm. The NH hydrogen atoms of the amido-thiophosphoryl groups appear at around $\delta = 10$ (**1**) or 11 (**2**) ppm. The values in each case are at lower fields than in the corresponding ligands ($\delta = 8.05$ ppm HL^1; 9.61 ppm HL^2). In the spectrum of **2** the shift of the other NH hydrogen atom ($\delta = 9.69$ ppm) also appears downfield of the corresponding shift in HL^2 ($\delta = 7.01$ ppm).

The ^{31}P{^{1}H} NMR spectra show two resonances, as expected, for the two nonequivalent phosphorous atoms. Those observed near $\delta = 50$ ppm can be assigned to the phosphorous atoms of the HL^1 or HL^2 coordinated fragments. In **1** the signal is $\delta = 2.6$ ppm upfield from that in

Table 1. Data for gold complexes **1**−**9**

Compound	Elemental Analysis[a]				Yield	Λ_M[b]	^{1}H NMR[c][d]	^{31}P{^{1}H}[c]
	C	H	N	S	(%)			
$[Au(L^1H)(PPh_3)]TfO$ (**1**)	41.65 (41.5)	3.55 (3.8)	1.75 (1.5)	10.15 (10.4)	78	160	1.36 (br. m, 12 H, *i*Pr-CH$_3$), 4.95 (br. m, 2 H, *i*Pr-CH), 7.20−7.79 (v.m., br, 20 H, Ph), 10.00 (br. s, 1 H, C-HN-P)	55.1 (s), 36.9 (s)
$[Au(L^2 H)(PPh_3)]TfO$ (**2**)	40.5 (40.85)	3.45 (3.85)	2.75 (3.0)	10.35 (10.2)	84	132	1.31−1.51 (v.m., br, 12 H, *i*Pr-CH$_3$), 4.85 (br. m, 2 H, *i*Pr-CH), 7.20−7.38 (v.m., br, 20 H, Ph), 9.69 (br. s, 1 H, C-HN-P), 10.83 (br. s, Ph-HN)	54.9 (s), 36.8 (s)
$[Au(L^1)(PPh_3)]$ (**3**)	47.65 (48.0)	3.95 (4.4)	1.3 (1.8)	7.95 (8.3)	58	1	1.26 (br. m, 12 H, *i*Pr-CH$_3$), 4.76 (br. m, 2 H, *i*Pr-CH), 7.20−7.47 (br. m, 20 H, Ph)	55.7 (s), 37.7 (s)
$[Au(L^2)(PPh_3)]$ (**4**)	46.85 (47.1)	4.05 (4.45)	3.15 (3.55)	7.65 (8.1)	48	3	1.25 (br. m, 12 H, *i*Pr-CH$_3$), 4.73 (br. m, 2 H, *i*Pr-CH), 7.24−7.58 (m., br, 20 H, Ph + 1 Ph-HN)	54.8 (s), 37.9 (s)
$[Au_2(L^1)(PPh_3)_2]TfO$ (**5**)	43.05 (43.4)	3.35 (3.55)	0.6 (1.0)	7.25 (6.95)	72	178	1.43 (br. m, 12 H, *i*Pr-CH$_3$), 4.92 (br. m, 2 H, *i*Pr-CH), 7.18 (v.m., br, 20 H, Ph)	49.4 (s), 36.2 (s)
$PPN[Au(L^1)_2]$ (**6**)	54.45 (54.4)	4.6 (5.0)	2.8 (3.05)	8.95 (9.35)	69	77	1.27 (br. m, 24 H, *i*Pr-CH$_3$), 4.83 (br. m, 4 H, *i*Pr-CH), 7.01−7.85 (v.m., br, 40 H, Ph)	63.1 (s)
$PPN[Au(L^2)_2]$ (**7**)	53.4 (53.85)	4.9 (5.05)	4.15 (4.05)	8.95 (9.25)	64	88	1.24 (br. m, 24 H, *i*Pr-CH$_3$), 4.80 (br. m, 4 H, *i*Pr-CH), 7.09−7.63 (v.m., br, 20 H, Ph), 8.52 (br. s, 2 H, Ph-HN-C)	63.7 (s)
$[Au(L^1)(C_6F_5)_2]$ (**8**)	35.55 (35.45)	2.5 (2.25)	1.55 (1.65)	7.5 (7.55)	54	2	1.25−1.48 (v.m., br, 12 H, *i*Pr-CH$_3$), 4.95 (br. m, 2 H, *i*Pr-CH), 7.36−8.14 (v.m., br, 5 H, Ph)	41.8 (s)
$[Au(L^2)(C_6F_5)_2]$ (**9**)	35.3 (34.8)	2.5 (2.35)	3.2 (3.25)	7.15 (7.45)	61	1	1.39 (br. m, 12 H, *i*Pr-CH$_3$), 4.82 (br. m, 2 H, *i*Pr-CH), 7.22−7.90 (v.m., br, 5 H, Ph + 1 Ph-HN)	43.5 (s)

[a] Calcd. values in parentheses. [b] $\Omega^{-1}cm^2mol^{-1}$. [c] δ in ppm. [d] v.m. means more than one multiplet.

the free ligand and in **2** it is shifted δ = 2.1 ppm downfield of that in free HL^2. The signal in the higher field region can be assigned to the triphenylphosphane ligand. In the Liquid Secondary Ion Mass Spectra (LSIMS +) of **2** the cation molecular peak can be observed at *m*/*z* = 792 (13 % intensity), although the most intense peak corresponds to the species $[Au(PPh_3)]^+$ (*m*/*z* = 459). The cationic molecular peak was not observed in the spectrum of **1** and the most intense peak corresponds to the species $[Au(PPh_3)]^+$ in this case also. An observation of note is the presence in both spectra of the peak corresponding to $[Au_2L(PPh_3)_2]^+$ which indicates the important stability of these species. This observation led us to specifically investigate the synthesis of complexes of higher nuclearity. The starting compound $[O\{Au(PPh_3)\}_3]^+$ is a good deprotonating agent which can also be used to introduce between one and three "Au(PPh$_3$)" fragments. The results of such reactions with both ligands in a 1:1 molar ratio are shown in Scheme 1. In both cases, the cleavage of the C=S bond and the formation of the corresponding *N*-[bis(isopropoxy)thiophosphoryl]benzamide [^{31}P{^{1}H} NMR: δ = 58.7(s)ppm] or *N*-[bis(isopropoxy)thiophosphoryl]-*N′*-phenylurea [^{31}P{^{1}H} NMR: δ = 58.2(s) ppm] and the gold complex $[S\{Au(PPh_3)\}_3]^+$ (^{31}P{^{1}H} NMR: δ: s, 33.4 ppm) were observed. Deprotonation of the ligands and coordination of only one "Au(PPh$_3$)" fragment is possible by using the starting compound [Au(acac)(PPh$_3$)] (acac = acetylacetonate). This reaction afforded $[AuL^1(PPh_3)]$ (**3**) and $[AuL^2(PPh_3)]$ (**4**). In the IR spectra of the latter complexes, the ν(P=S) vibrations appear at 584 and 577 cm^{-1}, respectively. The ν(NH) vibrations due to the "CN(H)P" fragments were not observed and in the spectrum of **4** the ν(NH) vibration corresponding to the "PhNH" unit appears at 3293 cm^{-1}. The ^{1}H NMR spectra also corroborate the observed deprotonation of the ligands since no signal corresponding to the "CN(H)P" fragment could be observed. In the spectrum of **4** the signal corresponding to the "PhNH" hydrogen atom overlaps with the broad signal arising from the protons of the PPh$_3$ group. The ^{31}P{^{1}H} NMR spectra of **3** and **4** show similar patterns to those observed in the spectra of **1** and **2**. It is of note that the chemical shifts observed for the thiophosphoryl phosphorous atoms are less significant compared with those of the analogous nondeprotonated complexes **1** and **2**. The signals corresponding to the triphenylphosphane ligands are shifted about 1 ppm downfield in both cases. In the LSIMS + the molecular peaks

Table 2. Data for silver complexes **10**−**17**

Compound	Analytical data[a]				Yield	Λ_M[b]	^{1}H NMR[c][d]	^{31}P{^{1}H}[c]
	C	H	N	S	(%)			
[Ag(TfO)(L^1H)] (**10**)	30.7 (29.3)	4.0 (3.5)	2.45 (2.45)	15.35 (16.75)	53	67	1.39 (br. m, 12 H, *i*Pr-CH_3), 4.89 (br. m, 2 H, *i*Pr-CH), 7.36−8.22 (v.m., br, 5 H, Ph + 1 C-HN-P)	52.2
[Ag(TfO)(L^2H)] (**11**)	29.0 (28.55)	4.0 (3.6)	4.5 (4.75)	15.05 (16.3)	78	72	1.40 (br. m, 12 H, *i*Pr-CH_3), 4.88 (br. m, 2 H, *i*Pr-CH), 7.37 (br. m, 5 H, Ph), 9.58 (br. s, 1 H, C-HN-P), 10.65 (br. s, Ph-HN)	54.0
[Ag(L^1H)(PPh_3)]TfO (**12**)	45.75 (45.95)	4.25 (4.2)	1.55 (1.65)	11.25 (11.5)	75	136	1.37 (br. m, 12 H, *i*Pr-CH_3), 4.99 (br. m, 2 H, *i*Pr-CH), 7.20−7.88 (m., br, 20 H, Ph), 11.57 (br. s, 1 H, C-HN-P)	53.7 (s), 15.3 (dd), 627.4, 543.9
[Ag(L^2 H)(PPh_3)]TfO (**13**)	45.35 (45.15)	4.05 (4.25)	3.65 (3.9)	10.95 (11.3)	94	132	1.19−1.40 (v.m., br, 12 H, *i*Pr-CH_3), 4.89 (br. m, 2 H, *i*Pr-CH), 7.20−7.38 (v.m., br, 20 H, Ph), 9.61 (br. s, 1 H, C-HN-P), 10.42 (br. s, Ph-HN)	54.8 (s), 14.5(dd), 617.9, 535.7
[Ag(L^1H)(PPh_3)$_2$]TfO (**14**)	54.2 (54.65)	4.35 (4.6)	1.1 (1.25)	7.3 (8.75)	85	155	1.33 (br. m, 12 H, *i*Pr-CH_3), 4.79 (br. m, 2 H, *i*Pr-CH), 7.21−7.62 (v.m., br, 35 H, Ph + 1 C-HN-P)	54.5 (s), 7.3 (br)
[Ag(L^2H)(PPh_3)$_2$]TfO (**15**)	53.8 (53.9)	4.45 (4.6)	2.4 (2.5)	7.44 (8.65)	84	140	1.38 (br. m, 12 H, *i*Pr-CH_3), 4.78 (br. m, 2 H, *i*Pr-CH), 7.12−7.31 (v.m., br, 35 H, Ph), 9.27 (br. s, 1 H, C-HN-P), 9.83 (br. s, 1 H, Ph-HN)	54.9 (s), 6.1 (dd), 409.8, 360.0
[Ag(L^1)(PPh_3)] (**16**)	53.65 (54.25)	4.8 (5.0)	1.95 (2.05)	9.05 (9.35)	66	1	1.27 (br. m, 12 H, *i*Pr-CH_3), 4.81 (br. m, 2 H, *i*Pr-CH), 7.22−7.61 (v.m., br, 20 H, Ph)	57.1 (s), 14.1 (dd), 570.3, 494.7
[Ag(L^2)(PPh_3)] (**17**)	52.65 (53.05)	4.45 (5.05)	3.55 (4.0)	8.75 (9.15)	54	1	1.21−1.49 (v.m., br, 12 H, *i*Pr-CH_3), 4.72 (br. m, 2 H, *i*Pr-CH), 6.94−7.68 (v.m., br, 20 H, Ph) + 1 Ph-HN)	58.4 (s), 14.3 (br)

[a] Theoretical values in brackets. [b] $\Omega^{-1}cm^2mol^{-1}$. [c] δ in ppm. [d] v.m. means more than one multiplet.

appear at *m*/*z* = 776 (16 %) (**3**) and 791 (8 %) (**4**). The reaction of HL^1 or HL^2 with [Au(TfO)(PPh_3)] in a 1:1 molar ratio in MeOH with a stoichiometric amount of KOH affords **3** or **4**. The reaction in a 1:2 molar ratio of HL^1 with [Au(TfO)(PPh_3)] in KOH/MeOH affords [$Au_2L^1(PPh_3)_2$]TfO (**5**). In the IR spectrum of **5** the vibrations corresponding to the anionic trifluoromethanesulfonate are observed and the ν(P=S) band appears at 579 cm^{-1}. The ligand deprotonation is confirmed by the absence of the NH vibration in the IR spectrum and an analysis of the ^{1}H NMR spectrum in which only those absorptions corresponding to the isopropyl and phenyl groups are observed. The ^{31}P{^{1}H} NMR spectrum display two signals, that at δ = 49.9 ppm can be assigned to the phosphorus atom of the thiophosphoryl group with the other (a broad signal) corresponding to the triphenylphosphane ligands. The cationic molecular peak is present in the LSIMS + (*m*/*z* = 1234, 52 %). The same reaction with HL^2 affords a solid, the ^{31}P{^{1}H} NMR spectrum of which displays five signals. The most intense resonance corresponds to the $[S\{Au(PPh_3)\}_3]^+$ cation and two of the signals which appear with very weak intensities at 54.9 and 37.0 ppm possibly correspond to the analog of **5** i.e. [$Au_2L^2(PPh_3)_2$]TfO. In fact, the LSIMS + shows a peak corresponding to the species [$Au_2L^2(PPh_3)_2$] (*m*/*z* = 1249, 28 %) and the proposed structure is shown in Scheme 1.

We have also investigated the reactivity of these ligands towards PPN[$Au(acac)_2$] in a molar ratio of 2:1. The resultant compounds PPN[$Au(L^1)_2$] (**6**) and PPN[$Au(L^2)_2$] (**7**) show ν(P=S) bands at 610 and 578 cm^{-1}, respectively. In **7** the ν(NH) vibration appears at 3302 cm^{-1}. The ^{1}H NMR spectra show the phenyl and isopropyl protons and in the case of compound **7** the NH hydrogen atom appears at δ = 8.52 ppm. Two signals are present in their ^{31}P{^{1}H} NMR spectra. The resonance at approximately δ = 63 ppm can be assigned to the thiophosphoryl group which shows a very significant downfield shift from the signals of the ligands. The other signal at δ = 21.2 ppm corresponds to the PPN cation. The anionic molecular peak of compound **6** is present in the LSIMS − (*m*/*z* = 829, 85 %). Although no structural confirmation has been obtained by X-ray crystallography, a homoleptic mononuclear derivative has been proposed. More complicated arrangements consisting of more that one "$[AuL_2]^+$" unit could give rise to the same conductivity and elemental analysis values but are considered to be much less probable. Based on the probable chelate mode of the ligand and the results of similar studies with other metals we are inclined to favor a tetra-coordinated arrangement as the most likely structure.

The syntheses of gold(III) complexes derived from [Au(acac)(C_6F_5)$_2$] have also been carried out. The resultant products, [Au(C_6F_5)$_2$(L^1)] (**8**) and [Au(C_6F_5)$_2$(L^2)] (**9**), show ν(P=S) vibrations at 567 and 591 cm^{-1}, respectively, and in **9** the ν(NH) vibration appears at 3403 cm^{-1}. The vibrations corresponding to the pentafluorophenyl rings are also present at around 1508, 964 and 784 cm^{-1}. In both derivatives the deprotonation of the ligands is evident from the ^1H NMR spectra. Very notable high field shifts from the values in the free ligands were observed in the $^{31}P\{^1H\}$ spectra for both complexes (see Table 1). The ^{19}F spectra show the presence of two nonequivalent pentafluorophenyl rings, five signals were observed in the ratio of 1(F_p):1(F_p):2(F_o):2(F_o):4(F_m). The signal at approximately δ = −160 ppm corresponds to the *meta* fluorine atoms. The fluorine atoms in the *para*- and *ortho*-positions give rise to two triplets at around δ = −158 ppm and two multiplets at approximately δ = −121 ppm, respectively. The molecular peaks are present in the LSIMS + at *m*/*z* = 848 (24 %) (**8**) and 863 (42 %; **9**).

Silver Complexes

The reaction of AgTfO with both ligands in a molar ratio of 1:1 afforded the complexes [Ag(TfO)(HL^1)] (**10**) and [Ag(TfO)(HL^2)] (**11**). Their conductivity values in acetone solution are between those described for the presence of no electrolyte and a 1:1 electrolytic species. This is due to the lability of the trifluoromethanesulfonate anion. In their IR spectra the vibrations corresponding to the presence of covalent TfO[26] groups are present [$\nu_{asym}(SO_3)$ 1283 and 1240, $\nu_{sym}(CF_3)$ 1220, $\nu_{asym}(CF_3)$ 1180, $\nu_{sym}(SO_3)$ 1030 cm^{-1}]. The ν(NH) and ν(P=S) vibrations appear at 3290, 575 (**10**) or 3270, 598 (**11**) cm^{-1}. In the ^1H NMR spectrum of **10** the NH hydrogen atom bonded to the thiophosphoryl group is coincidental with the multiplet which corresponds to the phenyl protons whereas in **11**, it appears at δ = 10.65 ppm. The other NH proton in **11** shows a resonance at δ = 9.58 ppm. Their $^{31}P\{^1H\}$ NMR spectra both display one singlet near δ = 50 ppm. These resonances are shifted upfield by δ = 5.5 ppm in (**10**) and downfield by δ = 1.2 ppm in (**11**) from those of the free ligands. The LSIMS + of complex **11** shows the cationic molecular peak [Ag(HL^2)]$^+$ at *m*/*z* = 441 (47 %).

Displacement of the trifluoromethanesulfonate anion and deprotonation in **10** and **11** allows the synthesis of different complexes. Thus, the reaction with triphenylphosphane in a 1:1 or 1:2 molar ratio affords the three-coordinate [Ag(HL^1)(PPh_3)]TfO (**12**), [Ag(HL^2)(PPh_3)]TfO (**13**) or four-coordinate [Ag(HL^1)(PPh_3)$_2$]TfO (**14**) and [Ag(HL^2)(PPh_3)$_2$]TfO (**15**) complexes. Compounds **12** and **13** can also be obtained by reaction of the ligands with [Ag(TfO)(PPh_3)] in a 1:1 molar ratio. In their IR spectra the vibrations corresponding to the TfO^- anion are present and those due to ν(P=S) appear at 575 (**12**) and 574 cm^{-1} (**13**). The NH bands appear at 3260 (**12**) or 3220 (**13**) cm^{-1}. In the ^1H NMR spectra, resonances arising from the hydrogen atoms of the NH groups bonded to the thiophosphoryl groups are shifted to low field from those of the free ligands. An additional signal is present in **13** at δ = 9.61 ppm due to the hydrogen atom of the NH urea unit. In the $^{31}P\{^1H\}$ NMR spectra the two nonequivalent phosphorus atoms display resonances with different shapes. One of them, assigned to the thiophosphoryl group, is a narrow resonance which appears at about δ = 54 ppm while the other is broad and corresponds to the triphenylphosphane ligand. When the spectra were recorded at −55 °C the broad resonances split into two doublets as a consequence of the phosphorus atom coupling to the two silver isotopes, ^{107}Ag and ^{109}Ag. The LSIMS + show the cationic molecular peaks in both cases [*m*/*z* = 686, 28 % (**12**); 704, 31 % (**13**)].

Like **12** and **13**, complexes **14** and **15** can also be obtained by reaction of the ligands with [Ag(TfO)(PPh_3)$_2$] in a 1:1 molar ratio. In their IR spectra the ν(P=S) vibrations appear at 571 (**14**) and 573 (**15**) cm^{-1}, and those arising from the NH groups come at 3280 (**14**) and 3220 (**15**) cm^{-1}. In the ^1H NMR spectra of **15** both the NH resonances can be observed whereas in **14** the resonance of the hydrogen atom of the NH group is obscured by the phenyl hydrogen resonances. The $^{31}P\{^1H\}$ NMR spectra show the same patterns observed for **12** and **13** but only in the case of **15** the broad signal becomes split at low temperature (even at −85 °C). For these four-coordinate complexes the resonances due to the triphenylphosphane ligands appear near δ = 7 ppm which is upfield of those in the three-coordinate analogs. The structure of both complexes have been analyzed by X-ray studies which reveal the expected four-coordination (tetrahedral geometry) around the silver center (Figure 1, Figure 2). In compound **14** the ring defined by Ag(1), S(1), P(1), N(1), C(1) and S(2) adopts a boat conformation in which the angle between the planes defined by S(1), P(1), Ag(1), S(2) and P(1), N(1), C(1), S(2) is 53.7°. Compound **15** shows a twist boat conformation in which the atoms S(1), Ag(1), S(2) and C(1) lie in the same plane. Similar Ag−P bond lengths (Tables 2 and 3) can be observed in both complexes which vary from 2.4712(8) to 2.4909(7) Å. The shortest values of those found in [Ag(dppe)$_2$]NO_3 [2.488(3)−2.527(3) Å][27] are very close to those in **14** and **15** and also those found in [Ag(phen){(PPh_2)$_2C_2B_{10}H_{10}$}]ClO_4 [2.463(2), 2.479(2) Å].[28] Longer values have been found in [Ag{($SPPh_2$)$_2CH_2$}{(PPh_2)$_2C_2B_{10}H_{10}$}]ClO_4 [2.526(2), 2.532(2) Å][28] and in [Ag(PPh_3)$_4$]ClO_4 (1 × 2.650(2), 3 × 2.668(5) Å).[29] Two different Ag−S bond lengths are present in each complex, the distances to the sulfur atoms of the thiophosphoryl groups are longer [2.6952(8) Å (**14**), 2.6648(8) (**15**) Å] than the other Ag-S distances [2.5892(2) Å (**14**), 2.5379(8) (**15**) Å] in both complexes (Table 4). These values can be compared with those found in other tetrahedral silver complexes such as [AgBr($18S_6$)] ($18S_6$ = 1,4,7,10,13,16-hexathiacyclooctadecane) [2.514(1)−2.636(1) Å],[30] [Ag{($SPPh_2$)$_2CH_2$}{(PPh_2)$_2C_2B_{10}H_{10}$}]ClO_4 [2.540(2), 2.588(2) Å],[28] [Ag{$S_2C_2(CN)_2$}(PPh_3)$_4$][31]

[2.568(7), 2.653(7) Å], or in [$Ag_4(\mu_3\text{-}SC_2B_{10}H_{11})_2(\mu\text{-}O_3SCF_3)_2(PPh_3)_2$][32] [two tetrahedral, two trigonal silver atoms, Ag(tetrahedral)−S distances 2.5467(14), 2.6508(14) Å].

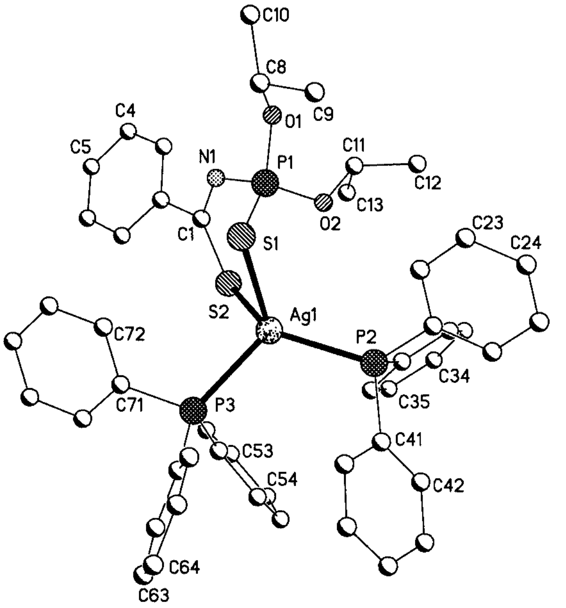


Figure 1. Molecular structure of the cation of compound **14**; hydrogen atoms have been omitted for clarity

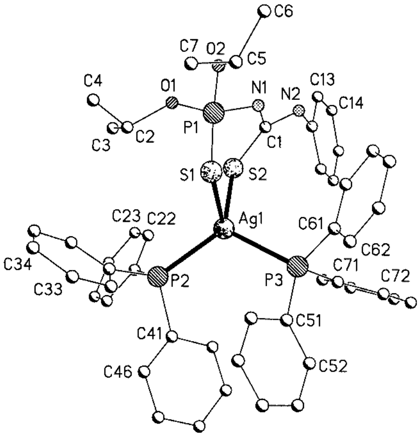


Figure 2. Molecular structure of the cation of compound **15**; hydrogen atoms have been omitted for clarity

Table 3. Selected bond lengths [Å] and angles [°] for **14**

Ag(1)−P(2)	2.4711(8)	N(1)−C(1)	1.355(3)
Ag(1)−P(3)	2.4907(7)	N(1)−P(1)	1.685(2)
Ag(1)−S(1)	2.5893(7)	P(1)−O(2)	1.550(2)
Ag(1)−S(2)	2.6954(7)	P(1)−O(1)	1.556(2)
S(1)−P(1)	1.9440(10)	S(2)−C(1)	1.666(3)
P(2)−Ag(1)−P(3)	116.11(2)	C(1)−S(2)−Ag(1)	114.36(10)
P(2)−Ag(1)−S(1)	117.50(2)	C(1)−N(1)−P(1)	128.2(2)
P(3)−Ag(1)−S(1)	115.56(2)	O(2)−P(1)−O(1)	106.61(11)
P(2)−Ag(1)−S(2)	117.29(2)	O(1)−P(1)−N(1)	99.81(11)
P(3)−Ag(1)−S(2)	90.74(2)	O(2)−P(1)−S(1)	112.25(8)
S(1)−Ag(1)−S(2)	94.48(2)	O(1)−P(1)−S(1)	115.66(9)
P(1)−S(1)−Ag(1)	92.47(3)	N(1)−P(1)−S(1)	114.52(9)

Table 4. Bond lengths [Å] and angles [°] for **15**

Ag(1)−P(2)	2.4510(8)	P(2)−C(41)	1.816(3)
Ag(1)−P(3)	2.4808(8)	P(2)−C(21)	1.820(3)
Ag(1)−S(2)	2.5379(8)	P(3)−C(51)	1.820(3)
Ag(1)−S(1)	2.6648(8)	P(3)−C(71)	1.824(3)
P(1)−O(1)	1.557(2)	P(3)−C(61)	1.827(3)
P(1)−O(2)	1.562(2)	S(2)−C(1)	1.682(3)
P(1)−N(1)	1.674(3)	N(1)−C(1)	1.368(4)
P(1)−S(1)	1.9390(10)	N(2)−C(1)	1.336(4)
P(2)−C(31)	1.814(3)	N(2)−C(11)	1.422(4)
P(2)−Ag(1)−P(3)	118.51(3)	O(1)−P(1)−O(2)	104.35(11)
P(2)−Ag(1)−S(2)	113.46(3)	O(1)−P(1)−N(1)	102.18(12)
P(3)−Ag(1)−S(2)	114.78(3)	O(2)−P(1)−N(1)	99.64(12)
P(2)−Ag(1)−S(1)	111.39(3)	O(1)−P(1)−S(1)	116.81(8)
P(3)−Ag(1)−S(1)	98.05(3)	O(2)−P(1)−S(1)	113.93(8)
S(2)−Ag(1)−S(1)	97.08(2)	N(1)−P(1)−S(1)	117.63(10)

The syntheses of deprotonated derivatives have been carried out by two synthetic routes just as for the gold complexes. The first is the use of $(acac)^-$ as a deprotonating agent, the other using methanol and KOH. The reactions afford [$AgL^1(PPh_3)$] (**16**) or [$AgL^2(PPh_3)$] (**17**). In the IR spectrum of **17** the ν(P=S) vibration appears at 575 cm^{-1} and the ν(NH) at 3203 cm^{-1}. Due to a poor mixture between **16** and Nujol, no satisfactory IR spectrum for **16** could be recorded. The deprotonation of the ligands is evident from the ^1H NMR spectra. Moreover, two resonances are present in the $^{31}P\{^1H\}$ NMR spectra and only in the case of compound **16**, the broad signal is split into two doublets.

Conclusions

The reactions studied indicate that a great variety of coordination types and complexes can be prepared (Schemes 1 and 2). Some notable points are a) The use of acetylacetonate as a suitable deprotonating agent. This is a new synthetic pathway that allows the use of solvents other than alcohols. The mixture MeOH/KOH, widely described in the literature, may not be the best since some metallic fragments may not be soluble in alcohol. b) The [Ag(HL)(TfO)] compounds synthesized are interesting starting materials which allow the incorporation of the "Ag(HL)" unit (also deprotonated) into more complicated structures. c) Cleavage of the C=S bond occurs upon the reaction of the oxonium salt [$O\{Au(PPh_3)\}_3$] with the ligands.

Experimental Section

Reagents: AgTfO and PPh_3 were purchased from Aldrich and were used as received. The ligands (HL^1)[4] and (HL^2)[5] and the starting materials [$Au(acac)(PPh_3)$],[33] [$O\{Au(PPh_3)\}_3$]ClO_4,[34] [$Au(acac)(C_6F_5)_2$],[35] PPN[$Au(acac)_2$],[33,36] [$Ag(TfO)(PPh_3)$],[37] [$Ag(TfO)(PPh_3)_2$][37] were synthesized according to literature methods. [$Au(TfO)(PPh_3)$] was synthesized from [$AuCl(PPh_3)$][38] and AgTfO in dichloromethane.

General Procedures: Infrared spectra were recorded on a Perkin−Elmer FT-IR Spectrum 1000 spectrophotometer in the range 4000−400 cm^{-1} using Nujol mulls between polyethylene sheets. Conductivities were measured in (ca. 5×10^{-4}) M acetone solutions with a Jenway 4010 conductimeter. Elemental analyses of C, H, N and S were carried out with a Perkin−Elmer 240C microanalyzer. Mass spectra were recorded on a VG Autospec instrument using the LSIMS (+, −) techniques and nitrobenzyl alcohol as a matrix and on an HP59987 A ELECTROSPRAY. ^{1}H, ^{19}F and ^{31}P NMR spectra were recorded on a Bruker ARX 300 spectrometer in $CDCl_3$ or $(CD_3)_2CO$. Chemical shifts are quoted relative to external $SiMe_4$ (^{1}H), $CFCl_3$ (^{19}F) or 85 % H_3PO_4 (^{31}P).

Syntheses: [Au(HL)(PPh$_3$)]TfO [L = L^1(1), L^2(2)]: HL^1 (0.1 mmol, 0.032 g) or HL^2 (0.1 mmol, 0.033 g) was added to a dichloromethane solution (20 mL) of [Au(TfO)(PPh$_3$)] (0.1 mmol, 0.0610 g). After stirring for 15 min the solvent was reduced to about 5 mL. Addition of *n*-hexane (20 mL) led to precipitation of an orange (**1**) or white (**2**) solid. Recrystallization from dichloromethane/hexane afforded the pure compounds.

[Au(L)(PPh$_3$)] [L = L^1(3), L^2(4)] Method a: KOH (0.1 mmol, 0.006 g) and then HL^1 (0.1 mmol, 0.032 g) or HL^2 (0.1 mmol, 0.033 g) was added to a solution of [Au(TfO)(PPh$_3$)] (0.1 mmol, 0.0610 g) in methanol (20 mL). After stirring for 15 min the solvent was reduced to about 5 mL. Addition of *n*-hexane (20 mL) led to precipitation of a yellow (**3**) or white (**4**) solid.

Table 5. Details of data collection and structure refinement for **14** and **15**

Compound	**14**	**15**
Chemical formula	$C_{50}H_{50}AgF_3NO_5P_3S_3$	$C_{50}H_{51}AgF_3N_2O_5P_3S_3$
Crystal habit	colorless prism	yellow tablet
Crystal size (mm)	0.5 × 0.2 × 0.14	0.32 × 0.28 × 0.2
Crystal system	monoclinic	triclinic
Space group	$P2_1/c$	$P\bar{1}$
a (Å)	22.0613(19)	12.9484(18)
b (Å)	12.8679(11)	13.3524(19)
c (Å)	18.8993(16)	15.831(2)
α (°)	90	71.895(2)
β (°)	113.755(1)	79.351(3)
γ (°)	90	76.764(2)
V (Å^3)	4910.6(7)	2513.3(6)
Z	4	2
D_c (g cm^{-3})	1.486	1.472
M_r	1098.87	1113.89
$F(000)$	2256	1144
T (°C)	−100	−100
$2\theta_{max}$ (°)	58	56
μ(Mo-K_α) (mm^{-1})	0.695	0.680
No. of reflections measured	31073	16548
No. of unique reflections	11287	11100
R_{int}	0.0769	0.0386
$R1$[a] [$F > 4\sigma(F)$]	0.0500	0.0446
$wR2$[b](F^2, all refl.)	0.1322	0.1006
No. of reflections used	11287	11100
No. of parameters	603	616
No. of restraints	0	0
S[c]	1.032	0.983
$\Delta\rho$ (Å^{-3})	2.026	1.222

[a] $R1\ (F) = \Sigma\|F_o| - |F_c\|/\Sigma|F_o|$. [b] $wR2\ (F^2) = [\Sigma\{w(F_o^2 - F_c^2)^2\}/\Sigma\{w(F_o^2)^2\}]^{0.5}$; $w^{-1} = \sigma^2(F_o^2) + (aP)^2 + bP$, where $P = [F_o^2 + 2F_c^2]/3$ and a and b are constants adjusted by the program. [c] $S = [\Sigma\{w(F_o^2 - F_c^2)^2\}/(n - p)]^{0.5}$, where n is the number of data and p the number of parameters.

Method b: HL^1 (0.1 mmol, 0.032 g) or HL^2 (0.1 mmol, 0.033 g) was added to a solution of [Au(acac)(PPh$_3$)] (0.1 mmol, 0.056 g) in dichloromethane. After stirring for 15 min the solution was filtered through celite and the filtrate concentrated to about 5 mL. Addition of *n*-hexane (20 mL) led to precipitation of a yellow (**3**) or white (**4**) solid**.** Recrystallization from dichloromethane/hexane afforded the pure compounds.

[Au$_2$(L^1)(PPh$_3$)$_2$]TfO (5): KOH (0.1 mmol, 0.006 g) and HL^1 (0.1 mmol, 0.032 g) were added to a solution of [Au(TfO)(PPh$_3$)] (0.2 mmol, 0.121 g) in methanol (20 mL). After stirring for 15 min the solvent was concentrated to about 5 mL. Addition of *n*-hexane (20 mL) led to precipitation of a yellow solid (**5**). Recrystallization from dichloromethane/hexane afforded the pure compound.

PPN[Au(L)$_2$] [L = L^1(6), L^2 (7)]: HL^1 (0.2 mmol, 0.064 g) or HL^2 (0.2 mmol, 0.066 g) was added to a solution of PPN[Au(acac)$_2$] (0.1 mmol, 0.093 g) in dichloromethane (20 mL). After stirring for 15 min the solution was filtered through celite and the filtrate concentrated to about 5 mL. Addition of *n*-hexane (20 mL) led to precipitation of a pale yellow (**6**) or brown (**7**) solid. Recrystallization from dichloromethane/hexane afforded the pure compounds.

[Au(C$_6$F$_5$)$_2$(L)] [L = L^1 (8), L^2 (9)]: HL^1 (0.1 mmol, 0.032 g) or HL^2 (0.1 mmol, 0.033 g) was added to a solution of [Au(C$_6$F$_5$)$_2$(acac)] (0.1 mmol, 0.063 g) in dichloromethane (20 mL). The stirred solution was filtered through celite and the filtrate concentrated to about 5 mL. Addition of *n*-hexane (20 mL) led to precipitation of a yellow solid (**8** or **9**). Recrystallization from dichloromethane/hexane afforded the pure compounds. ^{19}F NMR for **8**: δ = −160 (m, *m*-F, 4F), 156 (t, *p*-F, ^3J(FF) 20.0 Hz), 155.7 (t, *p*-F, ^3J(FF) 19.8 Hz), −121.9 (m, *o*-F, 2F), −121.7 (m, *o*-F, 2F) ppm. ^{19}F NMR for **9**: δ = −161.8 (m, *m*-F, 4F), 157.2 (t, *p*-F, ^3J(FF) 20.0 Hz), 156.8 (t, *p*-F, ^3J(FF) 19.6 Hz), −122.4 (m, *o*-F, 2F), −122.1 (m, *o*-F, 2F).

[Ag(HL)(TfO)] [L = L^1 (10), L^2 (11)]: HL^1 (0.1 mmol, 0.032 g) or HL^2 (0.1 mmol, 0.033 g) was added to a dichloromethane solution (20 mL) of Ag(TfO) (0.1 mmol, 0.026 g). After stirring for 4 hours the solvent was reduced to about 5 mL. Addition of *n*-pentane (20 mL) led to precipitation of a yellow (**10**) or white (**11**) solid. Recrystallization from dichloromethane/pentane afforded the pure compounds.

[Ag(HL)(PPh$_3$)]TfO [L = L^1 (12), L^2 (13)] Method a: PPh$_3$ (0.1 mmol, 0.026 g) was added to a solution of [Ag(HL)(TfO)] (0.1 mmol; L^1 0.057 g, L^2 0.058 g) in dichloromethane (20 mL). After stirring for 15 min the solvent was concentrated to about 5 mL. Addition of *n*-hexane (20 mL) led to precipitation of a yellow (**12**) or white (**13**) solid.

Method b: HL^1 (0.1 mmol, 0.032 g) or HL^2 (0.1 mmol, 0.033 g) was added to a solution of [Ag(TfO)(PPh$_3$)] (0.1 mmol, 0.052 g) in dichloromethane (20 mL). The stirred solution was concentrated to about 5 mL. Addition of *n*-hexane (20 mL) led to precipitation of a yellow (**12**) or white (**13**) solid. Recrystallization from dichloromethane/hexane afforded the pure compounds.

[Ag(HL)(PPh$_3$)$_2$]TfO [L = L^1 (14), L^2 (15)] Method a: PPh$_3$ (0.2 mmol, 0.053 g) was added to a solution of [Ag(HL)(TfO)] (0.1 mmol; L^1 0.057 g, L^2 0.058 g) in dichloromethane (20 mL). After stirring for 15 min the solvent was concentrated to about 5 mL. Addition of *n*-hexane (20 mL) led to precipitation of a yellow (**14**) or white (**15**) solid.

Method b: HL^1 (0.1 mmol, 0.032 g) or HL^2 (0.1 mmol, 0.033 g) was added to a solution of $[Ag(TfO)(PPh_3)_2]$ (0.1 mmol, 0.078 g) in dichloromethane (20 mL). The stirred solution was concentrated to about 5 mL. Addition of *n*-hexane (20 mL) led to precipitation of a yellow (**14**) or white (**15**) solid. Recrystallization from dichloromethane/hexane afforded the pure compounds.

$[Ag(L)(PH_3)]$ [L = L^1 (16), L^2 (17)] Method a: KOH (0.1 mmol, 0.006 g) and HL^1 (0.1 mmol, 0.032 g) or HL^2 (0.1 mmol, 0.033 g) were added to a solution of $[Ag(TfO)(PPh_3)]$ (0.1 mmol, 0.052 g) in methanol (20 mL). After stirring for 15 min the solvent was concentrated to about 5 mL. Addition of *n*-hexane (20 mL) led to precipitation of a pale yellow (**16**) or white (**17**) solid.
Method b: HL^1 (0.1 mmol, 0.032 g) or HL^2 (0.1 mmol, 0.033 g) was added to a solution of $[Ag(acac)(PPh_3)]$ (0.1 mmol, 0.047 g) in dichloromethane. The stirred solution was filtered through celite and the filtrate concentrated to about 5 mL. Addition of *n*-hexane (20 mL) led to precipitation of a pale yellow (**16**) or white (**17**) solid. Recrystallization from dichloromethane/hexane afforded the pure compounds.

X-ray Crystallographic Study: The crystals were mounted in inert oil on a glass fiber and transferred to the cold gas stream of a Bruker SMART APEX CCD system diffractometer. Data were collected using monochromated Mo-K_α radiation (λ = 0.71073 Å). Absorption corrections were based on multiple scans (program SADABS). The structures were refined on F^2 using the program SHELXL-97.[39] All non-hydrogen atoms were refined anisotropically. CCDC 203107 and 203108 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge at www.ccdc.cam.ac.uk/conts/retrieving.html [or from the Cambridge Crystallographic Data Center, 12, Union Road, Cambridge CB2 1EZ, UK; fax: (internat.) +44-1223/336-033; E-mail: deposit@ccdc.cam.ac.uk].

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