Reactions of Diaminophosphenium and 1,3,2-Diazaphospholenium Triflates with Silver Salts☆

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Reaction of bis(diisopropylamino)phosphenium triflate (**1**[CF_3SO_3]) with silver salts AgY [Y^- = $CF_3CO_2^-$ (**2a**), $CF_3SO_3^-$ (**2b**), $CH_3CO_2^-$ (**2c**)] affords neutral complexes [{(iPr$_2$N)$_2$(Y)P} Ag(OSO_2CF_3)] (**3a–c**). While **3a**, **c** are stable up to ambient temperature, **3b** is only stable at low temperature and in equilibrium with the cation **1**. The constitution of **3a–c** was derived from multinuclear (^{1}H, ^{13}C, ^{31}P, ^{109}Ag) NMR spectra. Compound **3a** was further studied by X-ray single-crystal diffractommetry which showed the presence of dimeric units with μ^2-bridging triflate ligands and three-coordinate silver atoms with a planar T-shaped coordination geometry. Reaction of 4-chloro-1,3-bis(2,6-dimethylphenyl)-1,3,2-diazaphospholenium triflate (**4**[CF_3SO_3]) with **2a**, **c** affords equilibrium mixtures whose ^{31}P- and ^{109}Ag-NMR spectra suggested the presence of silver complexes **5a**, **c** with constitutions similar to those of **3a**, **c** besides unreacted cation **4**. No reaction was observed between **4**[CF_3SO_3] and **2b**. A common mechanism accounting for the different outcome of the individual reactions will be discussed.

The ability of phosphenium ions R_2P^+ to form stable cationic transition-metal complexes of type **I** has long been recognised[1]. Considering that the free cations are isoelectronic and isolobal with neutral carbenes, the complexes **I** share the same relation with the carbene complexes **II** which are of considerable importance in organic and organometallic chemistry[2].

Scheme 1

$$L_nM{=}\overset{\oplus}{P}R_2 \qquad\qquad L_nM{=}CR_2$$

I II

However, whereas carbene complexes are known for most d-block transition metals, examples of phosphenium complexes have hitherto been restricted mainly to group 6 (Mo, W) and group 8 (Fe) metals; lately, a single nickel phosphenium complex was reported[3]. The recently renewed interest in carbene complexes of the coinage metals[4,5] stimulated us to investigate if similar phosphenium complexes of these metals can be obtained. Knowing that many phosphorus ligands form stable coordination compounds with Ag^+, we studied the reactivity of stable diaminophosphenium and 1,3,2-diazaphospholenium cations[6] (which can be regarded as the isolobal and isoelectronic counterparts to the stable imidazoyl carbenes[7]) towards silver salts AgY (Y^- = $CF_3SO_3^-$, $CF_3CO_2^-$, $CH_3CO_2^-$).

Reactions

Reaction of bis(diisopropylamino)phosphenium triflate (**1**[CF_3SO_3])[8] with one equivalent of CF_3CO_2Ag (**2a**) in CH_2Cl_2 afforded according to an ^{31}P-NMR spectroscopic assay a single product which was isolated in moderate yield as colourless, air- and moisture-sensitive crystals. The product was identified by NMR spectroscopy and by X-ray crystal structure analysis as the phosphane complex **3a** featuring a four-coordinate phosphorus centre, rather than an anticipated three-coordinate phosphenium complex. In contrast to the known behaviour of phosphanes and phosphites[9,10], no evidence for the formation of complexes of the type $[Ag(PR_3)_n]^+$ ($n > 1$) was obtained when **3a** was treated with an excess of phosphenium salt.

Similar reactions as with CF_3CO_2Ag were observed with **1**[CF_3SO_3] and CF_3SO_3Ag (**2b**) or CH_3CO_2Ag (**2c**). An ^{31}P-NMR spectroscopic assay of the reaction of equimolar amounts of the phosphenium salt and **2b** disclosed a marked temperature dependence of the spectra which suggested that a dynamic mixture of several equilibrating components had formed. Spectra under slow exchange conditions revealed at −110°C the presence of a mixture of **1** and a second species which displays very similar ^{31}P- and ^{109}Ag-NMR spectra as **3a** and was therefore assigned to the complex **3b** (Scheme 2). The relative signal intensities changed when the molar ratios of the reactants were varied, but no further products could be identified, and free **1** was still observed even in the presence of a twofold excess of the silver salt. The complex **3b** was isolated – albeit in low

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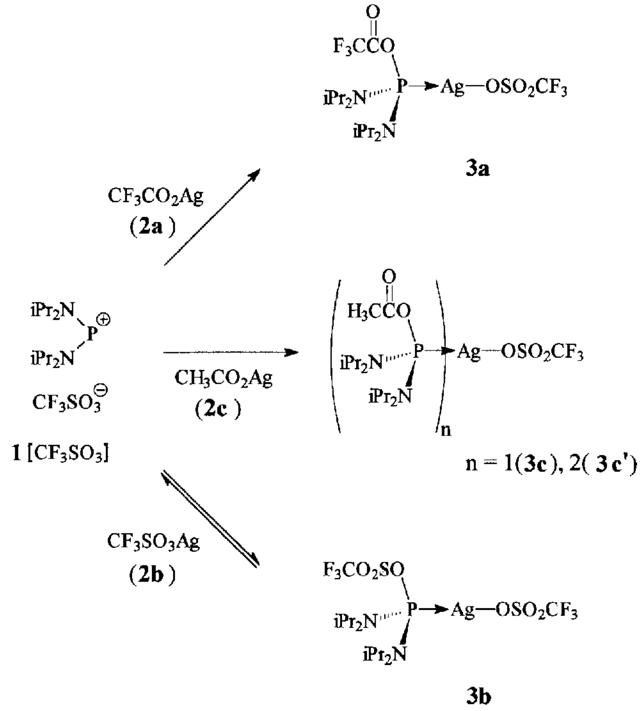
yield and in an impure form – by crystallisation from the reaction mixtures at −80 °C.

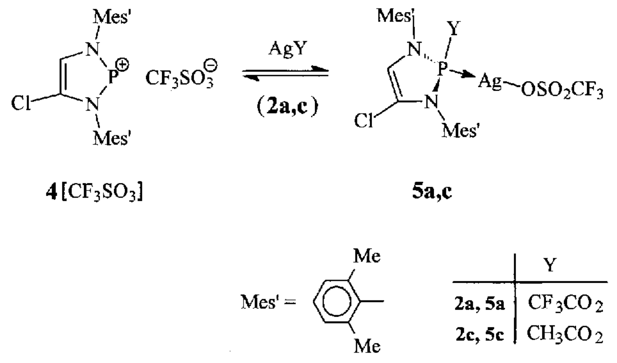
Treatment of $1[CF_3SO_3]$ with one equivalent of CH_3CO_2Ag furnished a mixture of two different silver complexes in a 9:1 molar ratio which were identified by multinuclear NMR spectroscopy as **3c** (major product) and **3c′** (Scheme 2). Unlike the previous reaction, no free **1** was detected by ^{31}P-NMR spectroscopy. Attempts at isolation of **3c, c′** failed due to the rapid onset of decomposition.

Scheme 2



In contrast to the acylic phosphenium salt, the 1,3,2-diazaphospholenium triflate $4[CF_3SO_3]$) which was prepared according to the procedure reported by Pudovik et al.[6] gave no detectable reaction with CF_3SO_3Ag between −100 and +30 °C. Treatment with CF_3CO_2Ag and CH_3CO_2Ag, which contain more nucleophilic anions, furnished solutions whose NMR-spectroscopic assay revealed the presence of equilibria between free **4** and silver complexes whose constitutions were assigned as **5a, c** based on the similarity of the observed NMR data to those of **3a–c** (Scheme 3). A remarkable feature of the reaction of $4[CF_3SO_3]$ with CH_3CO_2Ag is that NMR spectra recorded at −100 °C revealed the formation of a mixture of altogether five different silver complexes whose strongly overlapping ^{31}P-NMR signals could only be resolved in a $^{31}P,^{109}Ag$ correlated 2D spectrum. Due to both thermodynamic and kinetic instability, the formed complexes could not be isolated and were only characterised in situ by their ^{31}P- and ^{109}Ag-NMR data (Table 1).

Scheme 3



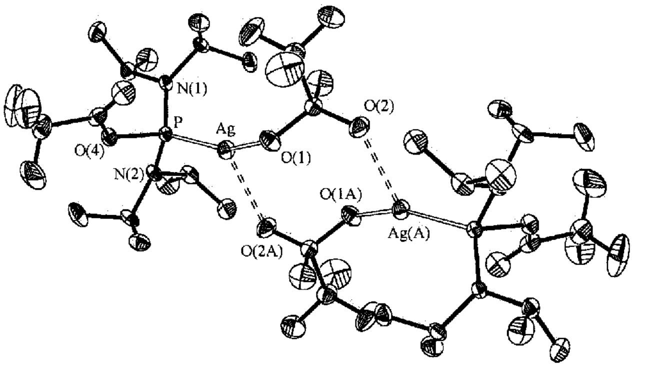
X-ray Crystal Structure of 3a

Complex **3a** crystallises in the space group $P\bar{1}$ with one formula unit per unit cell. The crystals contain dinuclear complexes which are formed by aggregation of two molecules of **3a** via additional "intermolecular" Ag–O bonds to give centrosymmetric dimers with a central $Ag_2S_2O_4$ eight-membered ring (Figure 1). As a result of the association, each triflate anion acts as an asymmetric μ^2-(η^1-O,η^1-O′)bridging ligand, and the silver atoms are three-coordinate. Both the two Ag–O bond lengths and the P–Ag–O angles differ considerably, the shorter "intramolecular" Ag–O(1) bond [2.244(3) Å] forming a larger angle [156.0(1)°] with the P–Ag bond and vice versa [Ag–O(2A) 2.416(3) Å, P–Ag–O(2A) 117.7(1)°]. This leads to an effectively planar [sum of angles 358.6(3)°], T-shaped coordination geometry at silver with very similar features as found previously in dinuclear complexes of the type $[(\mu^2\text{-}L\text{–}L)Ag(\mu^2\text{-}RCO_2)]_2$ (μ^2-L–L = bridging bisphosphane)[11], and in the cationic complex $[(L'^+)(thf)(CF_3SO_3)Ag]$ (L'^+ = bis(triphenylphosphonio)isophosphindole)[12]. As expected, the phosphorus in **3a** is connected to Ag, N(1), N(2), and the O(1) oxygen of the trifluoroacetate. The P–Ag [2.349(1) Å] and P–N bonds [1.627(3) and 1.663(3) Å] are somewhat shorter as those in $[\{(Me_2N)_3P\}_2Ag]^+$ [2.392–2.394 Å (P–Ag), 1.651–1.677 Å (P–N)[9]]. The P–O(4) bond [1.707(2) Å] is longer than expected [r(P–O) in phosphite complexes is in the range 1.60 ± 0.01 Å[13]], and while the O(1)–P–N(1)/N(2) angles [93.9(1) and 103.8(1)°] are smaller than the tetrahedral angle of 109.4°, the Ag–P–N(1)/N(2) angles are enlargened to 118.2(1) and 119.6(1)°. On the whole, the geometry at phosphorus appears as a distorted tetrahedron and resembles a very early state in a hypothetical reaction involving the conversion of a neutral tertiary phosphane complex into a cationic phosphenium complex via cleavage of the trifluoroacetate anion. A similarly distorted tetrahedral coordination was reported for the four-coordinate silicon atoms in donor-stabilised silylene complexes of the type $(CO)_nM{\leftarrow}SiR_2{\leftarrow}HMPT$[14], suggesting that **3a** may be likewise formulated as a Lewis acid/base complex of a cationic phosphenium complex with a trifluoroacetate anion.

NMR-Spectroscopic Investigations

Characterisation of **3a–c′** by $^{31}P,^{109}Ag$ shift-correlated 2D-NMR spectroscopy[15] revealed the presence of AX spin systems (A = ^{31}P, X = ^{109}Ag) in **3a–c** and an A_2X spin

Figure 1. ORTEP view (50%-probability ellipsoids) of crystalline **3a**[a]



[a] Selected bond lengths [Å] and angles [°]: Ag–P 2.3489(11), Ag–O(1) 2.244(3), Ag–O(2A) 2.416(3), P–N(1) 1.627(3), P–N(2) 1.663(3), P–O(4) 1.707(2); P–Ag–O(1) 156.03(7), P–Ag–O(2A) 117.75(7), O(1)–Ag–O(2A) 84.84(10), N(1)–P–Ag 118.23(10), N(2)–P–Ag 119.63(11), N(1)–P–N(2) 106.38(14), O(4)–P–N(1) 103.84(13), O(4)–P–N(2) 93.93(13).

system in **3c**′, thus indicating that the products may be formulated as 1:1 and 2:1 complexes with an "AgP" (**3a**–**c**) or "AgP_2" core (**3c**′). The occurrence of AX spin systems associated with an "AgP" core was also established for the three components of highest abundance formed in the reaction of **4**[SO_3CF_3] with CH_3CO_2Ag; a multiplicity analysis of the signals of the two remaining components was in this case prevented by unsufficient signal-to-noise ratio.

Table 1. ^{31}P- and ^{109}Ag-NMR data of the silver complexes **3a**–**c**′, **5a**, **5c** (in CH_2Cl_2)

	T [°C]	$\delta^{31}P$	$\delta^{109}Ag$	$^{1}J_{^{109}Ag,^{31}P}$
3a	-80	103.2	400.1	1140
3b	-110	121.3	433	1116
3c	-40	93.0	385	1191
3c'	-40	98.5	560	814
5a	-110	91.6	- [a]	1040 [b]
5c	-110	86.1 85.3 86.2 85.3 84.6	469 488 533 539 542	1119 1013 1004 975 999

[a] Not determined. – [b] $0.5 \cdot [J(^{107}Ag,^{31}P) + J(^{109}Ag,^{31}P)]$.

The observed ^{31}P-NMR data of all silver complexes (Table 1) bear close similarity to those of $[\{(Me_2N)_3P\}AgBF_4]$ [$\delta^{31}P$ 121.5, $J(^{109}Ag,^{31}P)$ 1047 Hz][9], suggesting that phosphane complexes with a four-coordinate phosphorus centre are present. In accord with this hypothesis is the observed diastereotopy of the methyl groups of the diisopropylamino substituents in the ^{1}H- (**3a**–**c**′) and ^{13}C-NMR (**3a**) spectra of **3a**–**c**′, which definitely rules out a planar three-coordination at phosphorus. A direct proof for the attachment of the (trifluoro)acetate as the fourth substituent to phosphorus in **3a** and **3c**, **c**′ was provided by the splitting of the carbonyl resonance in the ^{13}C-NMR spectrum of **3a** and the ^{1}H-NMR signal of the acetate protons in **3c**, **c**′ due to coupling with one (**3a**, **c**) and two (**3c**′) phosphorus nuclei, respectively. Even if the NMR data provided no positive evidence for a coordination of the remaining triflate anion to the silver atom, the results of the crystal structure analysis of **3a** suggest that this is most likely the case. The large magnitude of $^{1}J(^{109}Ag,^{31}P)$ and the high shielding of the silver nucleus in **3a** (see Table 1) as compared to known values for phosphane complexes ($\delta^{109}Ag$ = 410–1400[14]) suggest further than in solution dissociation[9] of the dinuclear species observed in the solid state into monomeric complexes with a dicoordinated silver may be of importance.

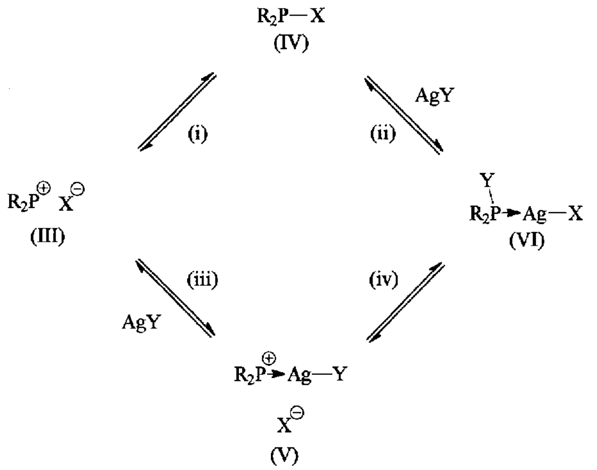
Inspection of the ^{31}P-NMR spectra of **3a** and **3c**, **c**′ indicated that no observable decomplexation of the phosphorus ligands occurred between −80 and 30 °C, and that any exchange processes were slow on the NMR time scale below 0 °C. In contrast, a sharp resonance for the complex **3b** was only observable besides the signal of the cation **1** at temperatures below −110 °C. Dynamic line broadening and finally coalescence of the two signals occurred when the temperature was successively increased to approx. −90 °C. At still higher temperatures, again an unexpected splitting of the average signal into two new resonances was observed, one appearing as a broad line centred at δ = 107 ± 3, while the position of the other one exhibited a considerable temperature dependence [$\delta^{31}P$ = 120 (−70 °C), 235 (+30 °C)]. The observed effects reveal that the solution must contain a mixture of several rapidly equilibrating components, however, since the ^{1}H- and ^{13}C-NMR spectra above −90 °C displayed only broad, unresolved average signals, no further structural elucidation was possible, and the nature of the individual species remains unknown.

The formation of several distinguishable 1:1 complexes in the reaction of **4**[CF_3SO_3] with CH_3CO_2Ag can be explained by assuming the presence of an equilibrium between monomeric **5c** and oligomeric aggregates. Owing to the chiral nature of the tetracoordinate phosphorus in the monomer, dimerisation affords two diastereomeric dinuclear complexes (**5c**)$_2$, thus accounting for three of the observed five products. The nature of the remaining species remains unclear; the assumption that they belong to "AgL_2" complexes with a similar structure than **3c**′ could not be ascertained from the 2D-NMR spectra.

Dicussion

The different outcome of the reactions of the cations **1** and **4** with the silver salts **2a**–**c** can be explained on the basis of the coupled equilibria depicted in Scheme 4. For pure **1**[CF_3SO_3], equilibrium (i) lies completely on the left side, and the ionic form **III** prevails[1,8]. The observed formation of **3a** from **1**[CF_3SO_3] and **2a** suggests that coordination of the cation **1** to silver [reaction (iii)] enhances the electrophilic character of phosphorus to such a degree that recombination of a ionic complex of type **V** affording the covalent product **VI** [reaction (iv)] is energetically favoured regardless of the low nucleophilicity of the triflate anion. Since stronger nucleophiles (e.g. Cl^-, acetate) shift equilibrium (i) to the right side even without the assistance of a transition metal, the reactions of **1**[CF_3SO_3] with **2b**, **c** may as well proceed via initial formation of the covalent intermediates **IV** [reaction (i), $X^- = CH_3CO_2^-$, $CF_3CO_2^-$] and subsequent coordination of a silver ion [reaction (ii)].

Scheme 4



Due to the delocalisation of the positive charge in the ring system[6], 1,3,2-diazaphospholenium ions are less electrophilic than diaminophosphenium ions[16]. As a consequence, a less pronounced tendency of the ionic species **III** and **V** towards the formation of the covalent products **IV** and **VI** can be expected, which would provide a consistent explanation for the incomplete conversion of **4** into the diazaphospholene complexes **5a, c** even in the presence of an excess of AgY. The failure to observe a reaction between **4**[CF_3SO_3] and CF_3SO_3Ag further suggests that equilibrium (iii) lies far on the left side, confirming that the studied cations are much weaker ligands towards Ag^+ than tertiary phosphanes.

Conclusions

In essence, the reported results demonstrate that the nature of the product of the reaction of a phosphenium salt with a transition metal is essentially determined by the way how the increased electron deficiency at phosphorus, which results from the formation of the dative phosphorus–metal bond, is compensated for. Thus, the capacity of the ML_n fragment to provide "intramolecular" electron transfer to phosphorus via back bonding from filled d-orbitals appears to be the decisive factor for the stability of known cationic phosphenium complexes **I** (Scheme 1). For metals with insufficient back bonding capabilities (Ag^+), "intermolecular" stabilisation is achieved by capture of an anion, resulting in the formation of neutral complexes which are structurally related to donor stabilised silylene complexes of the type $(CO)_4Fe{\leftarrow}SiR_2{\leftarrow}HMPT$[14]. To emphasise once more the analogy between phosphenium and carbene complexes, the metal-assisted association of **1** and $CF_3SO_3^-$ to give **3b** can be considered as the reversal of a "metal-assisted ionisation" of a carbenoid[17].

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Experimental

All manipulations were carried out under dry argon. Solvents were dried by using standard procedures. Silver salts were commercially available and were vacuum-dried prior to use. The synthesis of **1**[CF_3SO_3][8] was described elsewhere. 2-Chloro-1,3-bis(2,6-dimethylphenyl)-1,3,2-diazaphospholene (**6**) was prepared in 45% yield [m.p. 120 °C, ^{31}P NMR (CH_2Cl_2): $\delta = 146.8$. – $C_{18}H_{19}Cl_2N_2P$ (365.24): calcd. C 59.19, H 5.24, N 7.67; found C 59.08, H 5.19, N 7.62] in analogy to the method described by Pudovik et al.[18] for the 1,3-dicyclohexyl-substituted derivative. – NMR: Bruker AMX 300 (^1H: 300.13 MHz, ^{13}C: 75.46 MHz, ^{15}N: 30.41 MHz, ^{31}P: 121.5 MHz, ^{109}Ag: 13.97 MHz) and AC 200 (^{19}F: 188.4 MHz). ^{109}Ag chemical shifts and multiplicities of Ag_nP_m spin systems were determined from ^{31}P-detected $^{31}P,^{109}Ag$ HMQC spectra by using published pulse sequences[15]. Chemical shifts were referenced to ext. TMS (^1H and ^{13}C), $CFCl_3$ (^{19}F), CH_3NO_2 (^{15}N, $\Xi = 10.136767$ MHz), 85% H_3PO_4 (^{31}P, $\Xi = 40.480747$ MHz), and Ag^+_{∞} (^{109}Ag, $\Xi = 4.653623$ MHz); a positive sign denotes a shift to lower frequencies. Coupling constants are given as absolute values. – MS: Kratos Concept 1 H, EI (70 eV); molecular masses refer to the most abundant isotopes. – Melting points were determined in sealed capillaries.

General Procedure for the Reaction of 1[CF_3SO_3] with Silver Salts AgY (**2a–c**): 1.0 mmol of **1**[CF_3SO_3] and the appropriate amount of silver salt (0.5–2.0 equivalents) were dissolved in 8 ml of CH_2Cl_2. After stirring for 0.5–1 h, the resulting solution was subjected to multinuclear (^1H, ^{31}P, and two-dimensional $^{31}P,^{109}Ag$) NMR studies at temperatures between –120 and +30 °C. Reactions of **1**[CF_3SO_3] with equimolar amounts of **2a, c** proceeded with quantitative formation of the complexes **3a, c, c′**. Except for some line broadening resulting from intermolecular ligand exchange, no significant changes were observed between –80 and +30 °C. Reaction with **2b** yielded a mixture of **1** and **3b** (–110 °C); the temperature dependence of the ^{31}P-NMR spectra was described (see text). While **3a, b** could be isolated under suitable conditions (see below), **3c, c′** were only characterised in situ: ^1H NMR (CH_2Cl_2, –40 °C): **3c**: 3.61 [m, 4 H, $J(H,H) = 7$ Hz, $J(P,H) = 15$ Hz, NCH], 2.18 [d, $J(P,H) = 2$ Hz, 3 H, CH_3CO_2], 1.26 [d, $J(H,H) = 7$ Hz, 6 H] and 1.23 [d, $J(H,H) = 7$ Hz, 6 H] ($NCCH_3$); **3c′**: 2.21 [dd, $|J(P,H) + J(P',H)| = 3$ Hz, CH_3CO_2], the resonances of the C_3H_7 residue are overlapped by the more intense lines of **3c**. – ^{31}P- and ^{109}Ag-NMR data are listed in Table 1.

[Bis(diisopropylamino)trifluoracetatophosphane](trifluoromethanesulfonato)silver(I) (**3a**): 380 mg (1.0 mmol) of **1**[CF_3SO_3] and 221 mg (1.0 mmol) of CF_3CO_2Ag (**2a**) were dissolved in 8 ml of CH_2Cl_2. The resulting light yellow solution was stirred for 1 h, then cooled to –30 °C and kept at this temperature for several days. The separated crystals were collected by filtration and dried carefully in vacuo. Compound **3a** was obtained in approx. 30–40% yield as colourless, extremely air- and moisture-sensitive crystals which turned immediately black upon contact with air. Due to the extreme senstivity of the product satisfactory elemental analyses could not be obtained. $^{31}P\{^1H\}$- and ^{109}Ag-NMR data are listed in Table 1. – ^1H NMR (CH_2Cl_2, 0 °C): 3.5 [m, 4 H, $^3J(H,H) = 6.9$ Hz, $^3J(P,H) = 14$ Hz, CH], 1.1 [d, 6 H, $^3J(H,H) = 6.9$ Hz] and 1.06 [d, 6 H, $^3J(H,H) = 6.9$ Hz] (CH_3). – $^{13}C\{^1H\}$ NMR (CH_2Cl_2, 0 °C) 154.6 [d, $^2J(P,C) = 43.2$, CO], 120.0 [q, $^1J(F,C) = 318.3$ Hz, SCF_3], 114.0 [q, $^1J(F,C) = 286.2$ Hz, CCF_3], 46.9 [d, $^2J(P,C) = 8.4$ Hz, PNCH], 23.8 [d, $^3J(P,C) = 4.9$ Hz] and 22.6 (s) (CH_3). – ^{19}F NMR ($CH_2Cl_2/CDCl_3$, 20 °C): –76.2 (CCF_3), –78.2 (SCF_3).

[Bis(diisopropylamino)trifluoromethanesulfonatophosphane](trifluoromethanesulfonato)silver(I) (**3b**): 380 mg (1.0 mmol) of

1[CF_3SO_3] and 257 mg (1.0 mmol) of CF_3SO_3Ag were allowed to react as described. The solid which separated after storage of the solution at −80 °C for several days was collected by filtration and dried in vacuo to give a white, crystalline product which exhibited a similar sensitivity towards moisture and air as **3a**. A ^{1}H-NMR spectroscopic assay showed that the isolated product contained 5−10% of [$i$$Pr_2NH_2$][$CF_3SO_3$] which was apparently formed by partial hydrolysis of **3a** and could not be separated. ^{31}P- and ^{109}Ag-NMR data of **3a** are listed in Table 1. − ^{1}H NMR (CH_2Cl_2, −110 °C): 3.60 (m, broad, 4H, NCH), 1.25 [d, J(H,H) = 7 Hz, 12H] and 1.23 [d, J(H,H) = 7 Hz, 12H] (CH_3). − ^{19}F NMR (CH_2Cl_2, 20 °C): −77.8.

4-Chloro-1,3-bis(2,6-dimethylphenyl)-1,3,2-diazaphospholenium Trifluoromethanesulfonate (**4**[CF_3SO_3]): 4.00 g (18 mmol) of $CF_3SO_3SiMe_3$ was added by means of a syringe to a solution of 6.41 g (18 mmol) of **6** in 16 ml of CH_2Cl_2. After stirring for 1 h, all volatile components were removed in vacuo. The residue was dissolved in 30 ml of CH_2Cl_2, and the product precipitated by addition of hexane. The precipitate was collected by filtration, washed twice with 10 ml of hexane and dried in vacuo. **4**[CF_3SO_3] was obtained in 85% yield as a colourless, microcrystalline solid which was extremely moisture-sensitive and decomposed rapidly upon contact with air. Due to the high sensitivity no satisfactory elemental analyses were obtained. − M.p. 172 °C (dec.). − ^{31}P{^{1}H} NMR (CH_2Cl_2): 202.5; ^{1}H NMR ($CDCl_3$): 8.10 (s, 1H, =CH−), 7.40−7.10 (m, 6H, C_6H_3), 2.24 (s, 6H) and 2.17 (s, 6H) (CH_3). − ^{13}C{^{1}H} NMR ($CDCl_3$): 135.71 [d, J(PC) = 3.8 Hz] and 134.52 [d, J(PC) = 3.7 Hz] (i-C, arom.), 134.46 [d, J(P,C) = 5.8 Hz] and 131.14 [d, J(P,C) = 6.7 Hz] (o-C, arom.), 133.59 [d, J(P,C) = 1.6 Hz, =CH−], 132.15 (d, J(P,C) = 1.2 Hz) and 131.69 [d, J(P,C) = 1.0 Hz] (m-C, arom.), 131.90 (s, =CCl−), 130.01 (s, p-C, arom.), 120.84 [q, J(F,C) = 320.6 Hz, CF_3], 18.27 [d, J(P,C) = 1.3 Hz] and 18.02 [d, J(P,C) = 1.7 Hz] (CH_3). − ^{15}N NMR (CH_2Cl_2/C_6D_6): −151.2 [d, ^1J(P,N) = 76.7 Hz], −154.7 [d, ^1J(P,N) = 79.3 Hz]. − ^{19}F NMR ($CDCl_3$): −77.8. − MS: m/e (%): 329 (4) $[M]^+$, 134 (100) $[C_6H_3Me_2NCH_3]^+$.

General Procedure for the Reaction of 4[CF_3SO_3] with Silver Salts AgY (**2a−c**): Reactions of **4**[CF_3SO_3] with **2a−c** were performed as described for **4**[CF_3SO_3]. According to the NMR spectra, reactions with **2a**, **c** gave dynamic equilibrium mixtures whose low-temperature spectra (−80 to −110 °C) revealed the presence of unreacted **4** together with products which were assigned to the silver complexes **5a**, **c** (see text). Attempts to isolate any products by low-temperature crystallisation failed. No reaction at all was observed between **4**[CF_3SO_3] and **2b**.

Crystal Structure Determination of **3a** *at 173(2) K:* Colourless needles [$C_{30}H_{56}Ag_2F_{12}N_4O_{10}P_2S_2$], M = 1202.6, crystal size 0.8 × 0.4 × 0.3 mm, triclinic, space group $P\bar{1}$ (No. 2): a = 8.323(3), b = 10.622(3), c = 13.476(3) Å, α = 101.29(2), β = 91.36(3), γ = 92.70(3)°, V = 1166.4(6) Å^3, Z = 1, ρ(calcd.) = 1.712 Mg m^{-3}, $F(000) = 608$, $\mu = 1.10$ mm^{-1}. 5100 reflections were collected with an Enraf-Nonius MACH3 diffractometer (Mo-K_α radiation, graphite monochromator) in the range $5° \leqslant 2\Theta \leqslant 53°$ ($-10 \leqslant h \leqslant 0$, $-13 \leqslant k \leqslant 13$, $-16 \leqslant l \leqslant 16$). 4755 independent reflections (R_{int} = 0.022) were used for the solution (SHELXS-86, direct methods) and refinement [SHELXL-93, full-matrix least squares on F^2, 288 parameters without restraints, non-hydrogen atom anisotropic, hydrogen atoms with a "riding"-model]; wR^2 = 0.124 (all data), R = 0.039 [$I > 2\sigma(I)$]. A semiempirical absorption correction from Ψ-scans was applied (max. and min. correction 0.999 and 0.980).

Further details on the crystal structure investigation are available on request from the Fachinformationszentrum Karlsruhe, D-76344 Eggenstein-Leopoldshafen, on quoting the depository number CSD-404668, the names of the authors, and the journal citation.

☆ Dedicated to Professor Dr. *Marianne Baudler* on the occasion of her 75th birthday.

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