[Bis(phosphonio)isophosphindolide]silver Complexes☆

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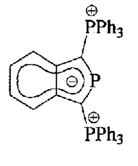
The outcome of reactions of bis(phosphonio)isophosphindolide salts **1**[X] and **6**[X] ($X^- = Cl^-, Br^-, CF_3SO_3^-$) with silver salts AgY ($Y^- = CF_3SO_3^-, CF_3CO_2^-, CH_3CO_2^-, 1/2\ SO_4^{2-}$) depends strongly on the available anions X, Y. If $X^-, Y^- = CF_3SO_3^-$, both mononuclear and dinuclear silver complexes are formed which exhibit either μ^1,η^1(P) or μ^2,η^1(P) coordination of the cations **1**, **6** to one or to both metals. In solution, dynamic equilibria between both types of products and free **1**, **6** were detected by ^{31}P-NMR spectroscopy. Mononuclear (**4a**, **7**) and dinuclear (**5a**, **8**) complexes were isolated as solvates with $CHCl_3$ or THF. If $X^-, Y^- = CF_3CO_2^-$, only equilibrium mixtures between the free ligands and silver complexes and no isolable products were obtained. ^{31}P-NMR investigations revealed a preference for the formation of dinuclear complexes. Anion metathesis and precipitation of AgX were observed for $X^- = Cl^-, Br^-$. No coordination of **1**, **6** to Ag^+ took place in the case of $Y^- = CH_3CO_2^-, SO_4^{2-}$. The formed complexes were characterised in solution by ^{31}P- and in part by ^{109}Ag-NMR spectroscopy. Complexes **7**, **8** were further studied by single crystal X-ray diffraction which revealed the presence of a THF molecule coordinated to silver in both cases. The μ^2-coordinated cation **1** is the only bridging ligand in **8**, whereas the presence of additional μ^2-CF_3CO_2 ligands was deduced from the results of ^{31}P,^{31}P EXSY measurements in the case of the trifluoroacetato complexes.

The electronic structure of the bis(triphenylphosphonio)isophosphindolide cation **1**[1] can be described in terms of a benzophospholide anion which exhibits a delocalised 10π-electron system extending over both fused rings, and two single-bonded, positively charged phosphonium substituents[2] (Scheme 1).

Scheme 1



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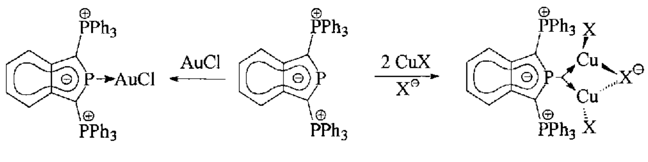
The spectroscopic properties and chemical reactivities of **1** are strongly determined by the balanced amphiphilic character of the two-coordinate phosphorus atom which shows both nucleophilic and electrophilic properties[1,2], similar to the phosphorus in a phosphenium cation[3], R_2P^+. However, as compared to the latter, the phosphorus centre in **1** behaves at the same time as a *weaker* electrophile and a *stronger* nucleophile, making bis(phosphonio)isophosphindolide cations potentially interesting ligands for transition-metal complexes. During our recent investigations of the coordination chemistry of **1**, we established that the cation may indeed act as a ligand towards coinage metals[4–6]. Depending on the nature of the metal, either mononuclear (**2**) or binuclear complexes (**3**) were formed (Scheme 2). Whereas **2** represents a typical phosphenium complex[3], the bonding situation in the Cu_2P unit of **3** was described in analogy to the case of organometallic arylcopper compounds[7] as a 2-electron-3-centre bond resulting from L(σ)→M electron transfer from the phosphorus "lone pair" with additional stabilisation by interactions between the metals and the ligand π-system[5]. Concerning its ligand properties, the bis(phosphonio)isophosphindolide ligand in **3a**, **b** thus constitutes a transition between a unique phosphenium cation and a phospholide anion[5]: whereas the former occurs exclusively as a 2-electron donating ligand, the latter is known to be able to bridge two metal centres in a μ^2,η^1(P) coordination mode, forming 2 electron-precise phosphorus–metal bonds and thus acting as a 4-electron donor[8].

Scheme 2



2 **1** X = Cl (**3a**), Br (**3b**)

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The diversity of the coordination behavior of **1** towards gold(I) and copper(I) which becomes evident from the different molecular constitutions of the complexes **2** and **3a, b** prompted us to investigate the reactivity of **1** towards the third group-12 metal, silver(I). The results of these studies are reported in this work.

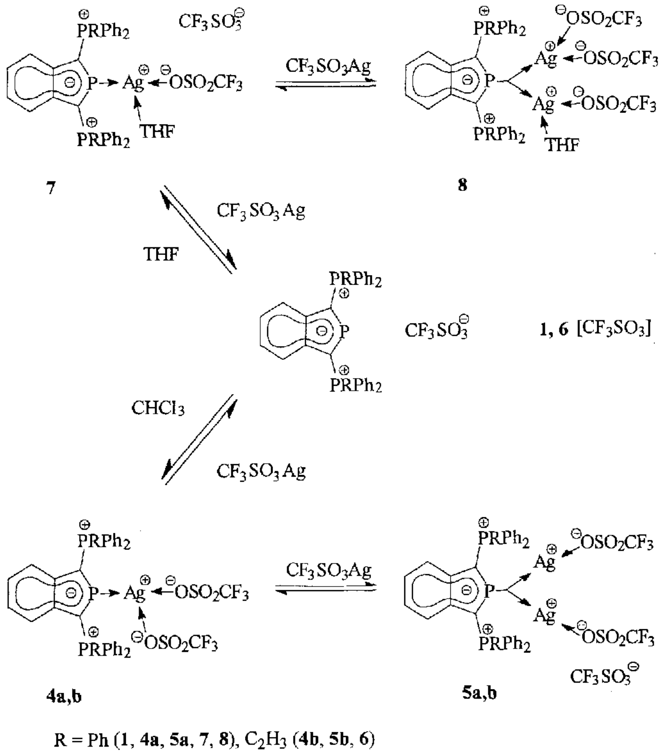
Reaction of Bis(phosphonio)isophosphindolide Salts with Ag(I) Compounds

In contrast to the clean formation of the complex **2** from **1**[CF_3SO_3] and AuCl[4], the reaction of equimolar amounts of **1**[Cl] and CF_3SO_3Ag in CH_2Cl_2 solution proceeded via anion metathesis and yielded a precipitate of AgCl together with **1**[CF_3SO_3][4] which was identified by comparison of its ^{31}P- and ^{19}F-NMR spectra with those of an authentic sample. The formation of silver complexes of **1** was only observed when CF_3SO_3Ag was added in axcess to the reaction mixture. The course of the reaction was easily monitored by following the changes in the ^{31}P-NMR spectra. At ambient temperature, with increasing concentration of the silver salt a continuous shift of the resonance of the two coordinate-phosphorus to higher field together with a marked line broadening and a decrease of the value of $^2J_{PP}$ was observed. Cooling to -50 °C produced a decoalescence of the spectrum into three separate sets of resonances. One of these was easily recognised as belonging to **1**, while the two others were assigned to the silver complexes **4a** and **5a** (Scheme 3) on the basis of the observed $^{107/109}$Ag,^{31}P coupling patterns (the number and character of the additional ligands at the silver atoms were postulated on the basis of the results of further spectroscopic studies and crystal structure determinations; see below). Comparison of the ^{31}P-NMR spectra of mixtures obtained by reaction of **1**[Cl] with 1.2 to 3.5 equivalents of CF_3SO_3Ag indicated that the variation of the metal-to-ligand (M/L) ratio produced concomitant changes in the molar ratios of free **1** and the complexes **4a** and **5a**, but that no further phosphorus-containing products were formed. The relative concentration of **4a** reached a maximum (approx. 70% of all phosphorus-containing products according to integration of the ^{31}P-NMR signals) at a M/L ratio of approximately 1:1, while higher M/L ratios favoured the formation of **5a**. The bis(vinyldiphenylphosphonio)isophosphindolide bromide, **6**[Br][2], displayed the same reaction behaviour towards CF_3SO_3Ag as **1**[Cl]; according to a ^{31}P-NMR spectroscopic assay, in this case the complexes **4b** and **5b** were formed.

The hypothesis that in the formed silver halide is not involved in the complexation reaction was confirmed by the outcome of the reaction of **1**[CF_3SO_3] with CF_3SO_3Ag. In this case, no precipitate was formed, and a ^{31}P-NMR spectroscopic assay revealed that solutions of exactly the same composition were obtained both by the reactions of **1**[CF_3SO_3] with one and of **1**[Cl] with two equivalents of CF_3SO_3Ag.

Despite the presence o dynamic equilibria between several species in all investigated reaction mixtures, solvates (with $CHCl_3$) of pure mono- and disilver complexes **4a**, **5a** could be readily isolated by crystallisation from solutions obtained by mixing stoichiometric quantities of **1**[CF_3SO_3] and CF_3SO_3Ag in $CHCl_3$. In a similar manner, the THF complexes **7** and **8** (Scheme 3) were accessible when the reaction was carried out in THF solution under otherwise identical conditions. The uniform composition of the products was checked by solid-state ^{31}P-NMR spectroscopy which indicated that in all cases only a single species was present (isotropic chemical shifts and values of $^1J_{Ag,P}$ are given in the experimental part; a duplication of the resonances for **7** was attributed to the occurrence of two crystallographically independent molecules. A full account of the results will be published elsewhere[9]). The constitution of the THF complexes **7** and **8** was inferred from single-crystal X-ray diffraction studies. In the case of **5a**, only single crystals of limited quality could be obtained whose final structure solution was prevented by the fact that the severe disorder present in part of the structure could not be satisfactorily resolved. Nonetheless, the available data confirmed the presence of dinuclear units of the composition [(μ^2-**1**)$Ag_2(OSO_2CF_3)_2$]$^+$ (see Scheme 3) as well as free triflate anions; the cations are further aggregated in a chain-like structure via the formation of additional intermolecular Ag−O contacts. All attempts to isolate **4b**, **5b** in a similar way as **4a** and **5a** failed; as the only result, ^{31}P-NMR spectroscopic studies revealed that a slow decomposition of the solutions took place. The results of further ^{31}P- and ^{109}Ag-NMR investigations of the complexes **4**, **5**, **7**, **8** will be discussed in more detail in a later section.

Scheme 3



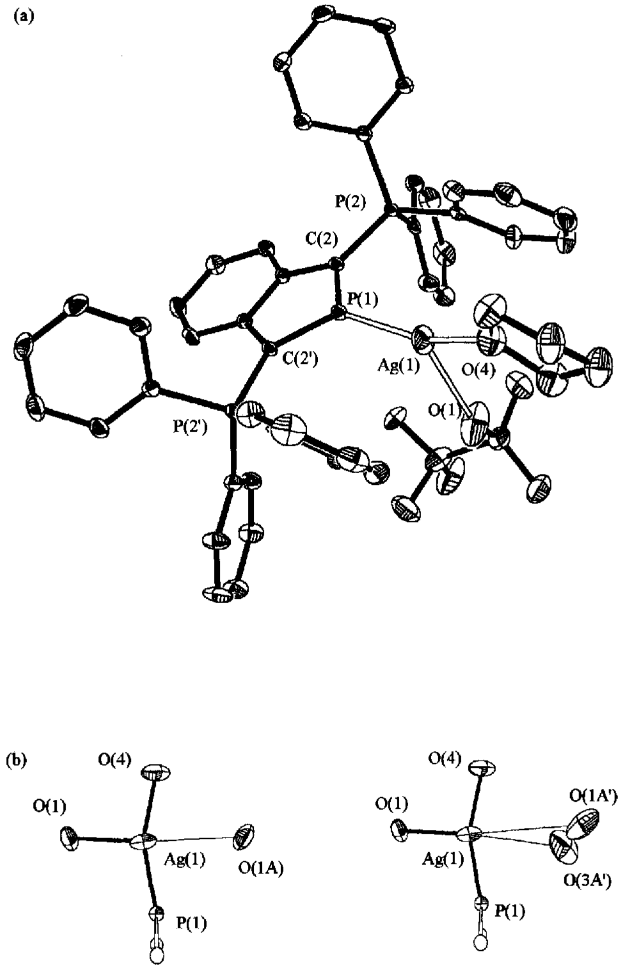
R = Ph (**1**, **4a**, **5a**, **7**, **8**), C_2H_3 (**4b**, **5b**, **6**)

The different behaviour of **1**[Cl] and **1**[CF_3SO_3] towards CF_3SO_3Ag stimulated us to study the role of the anions during the formation of bis(phosphonio)isophosphindolide–silver complexes in more detail. Thus, $1[CF_3SO_3]$ was allowed to react with equimolar quantities of Ag_2SO_4, CH_3CO_2Ag, and CF_3CO_2Ag, and the obtained solutions were investigated by ^{31}P-NMR spectroscopy. Treatment of $1[CF_3SO_3]$ with Ag_2SO_4 in CH_2Cl_2/MeOH (1:1) caused no change at all in the ^{31}P-NMR spectra, indicating that no silver complexes of **1** had formed. With CH_3CO_2Ag, a slight upfield shift and some line-broadening of the resonance of the two-coordinate phosphorus in **1** were detected, suggesting that the free cation may be in equilibrium with a small amount of a silver complex. No decoalescence of the signals at low temperature was observed, however, thus preventing the further identification of the complex. Finally, addition of solid CF_3CO_2Ag to a CH_2Cl_2 solution of $1[CF_3SO_3]$ resulted only in partial dissolution of the silver salt. A ^{31}P-NMR spectroscopic assay of the supernatant reddish solution at −80 °C revealed the presence of an equilibrium mixture whose major phosphorus-containing components were identified as free **1** and a dinuclear silver complex which exhibits a μ^2(P)-coordinated cationic ligand similar to **5a**; furthermore, traces of a monosilver complex were also detected. The appearance of the spectra remained unchanged when the silver salt was added in excess. Again, very similar results were obtained when $1[CF_3SO_3]$ was replaced by salts containing the cation **6**. The isolation of any of the formed complexes was prevented by the limited stability of the solutions which undergo extensive decomposition within a few hours.

X-ray Crystal Structures of 7 and 8

Complex **7** crystallises in the space group *C*2/*c* with three molecules of THF per formula unit. Two of these refer to solvent molecules which exhibit only van-der-Waals contacts to their next neighbours. The third THF and the cation **1** are coordinated to the silver via their oxygen and phosphorus atoms, respectively. Both ligands occupy special positions on the crystallographic two fold axis, while the metal itself as well as the triflate anions are each disordered between two independent positions with respect to the same axis. As a consequence of this disorder, four distinguishable conformations for a particular molecule of **7** can be contrived. Inspection of the individual Ag–O distances revealed in two of the four conformers the presence of a single, exceptionally short contact of 2.387(9) Å which lies in the range of a bonding interaction. All other distances range between 3.21 and 3.81 Å and thus exceed the sum of the van-der-Waals radii (3.20 Å[10]). If we assume that the unique short Ag–O distance corresponds to a real bond which connects two atoms in the same molecule and neglect the two other arrangements of atoms, only two possible molecular conformations remain. Both of these are composed of separate $[(1)Ag(thf)(OSO_2CF_3)]^+$ cations (see Figure 1a) and $CF_3SO_3^-$ anions, and differ only in the orientation of the two fragments relative to each other (Figure 1b).

Figure 1. (a) ORTEP view (50% probability ellipsoids) of the $[(1)Ag(thf)(CF_3SO_3)]^+$ cation in crystalline **7**; (b) reduced representation of the coordination spheres of the silver and phosphorus atoms in the two symmetry-inequivalent arrangements of the silver atoms and $CF_3SO_3^-$ anions[a]



[a] Selected bond lengths [Å] and angles [°]: Ag(1)–P(1) 2.338(1), Ag(1)–O(4) 2.238(4), Ag(1)–O(1) 2.387(9), P(1)–C(2) 1.715(3), Ag(1)–O(1A) 3.21, Ag(1)–O(1A'), 3.81, Ag(1)–O(3A') 3.61, P(1)–Ag(1)–O(4) 159.2(1), P(1)–Ag(1)–O(1) 103.3(3), O(1)–Ag(1)–O(4) 97.5(3), C(2)–P(1)–C(1A) 93.8(2), C(2)–P(1)–Ag(1) 132.3(1).

The silver in the complex cation displays a planar T-shaped coordination with a slight distortion towards trigonal geometry. The two bonds adjacent to the unique large P–Ag–O bond angle [159.2(1)°] which form the "bar" of the T are shorter [Ag–P 2.338(1), Ag–O 2.238(4) Å] than the third bond to the η^1(O)-bonded triflate [Ag–O 2.387(9) Å]. As in the copper complex **3b**[5], the metal coordination plane and the ring plane of the isophopshindole unit are almost orthogonal (dihedral angle 92.3°). The encapsulation of the silver atom by the two PPh_3 moieties matches typical features of **2**[4] and **3b**[5]. Likewise, the occurrence of two short contacts (2.98 and 3.11 Å) between the metal and carbon atoms of the adjacent phenyl rings with distances well below the sum of the van-der-Waals radii (3.40 Å[10]) should as in the case of the gold complex **2**[4] be considered a consequence of steric crowding rather than a weak bonding interaction.

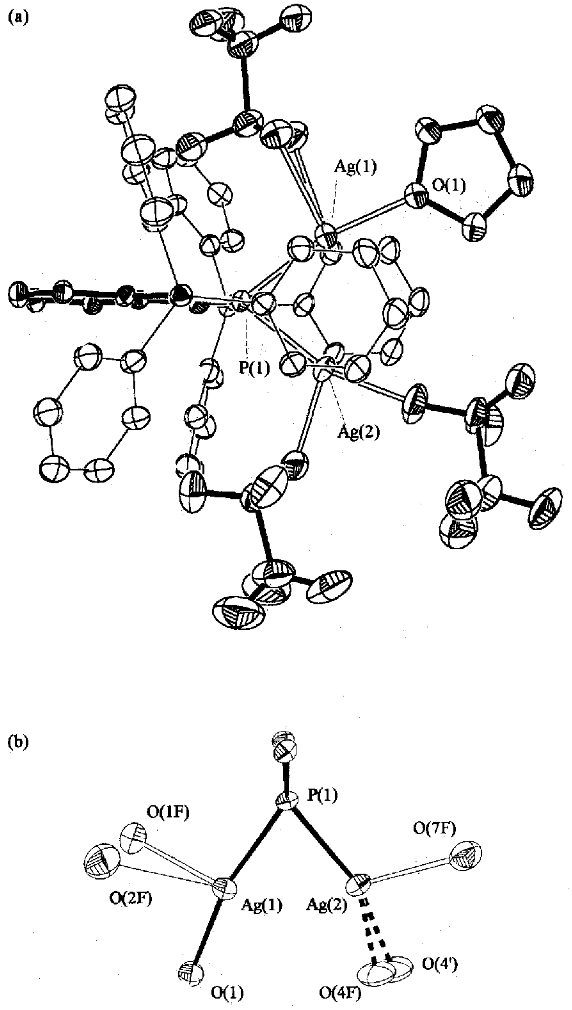
The Ag–P distance in **7** lies at the lower end of the range of silver–phosphorus bond lengths in related complexes of tertiary phosphanes[11–13]. In contrast to the perfectly planar geometry at the oxygen in the THF ligand [sum of bond angles 360(9)°], the metal-bonded phosphorus exhibits a weak but distinct pyramidal distortion [sum of angles 358.3(4)°] which is of similar extent as in the gold complex **2**[4]. As in the case of **2** and **3b**, the structural parameters of coordinated **1** show no significant deviations from those of the free ligand[4].

The crystal structure determination of the disilver complex **8** revealed the presence of two independent molecules and ten THF molecules per asymmetric unit. One molecule of **8** is shown in Figure 2a. The second one, whose bond data are given in brackets in the following discussion, differs mainly in the arrangement of the triflate ligands and the torsional angles of the phenyl moieties in the PPh_3 groups.

The reduced view (Figure 2b) of the coordination sphere of the two silver atoms reveals the absence of any further bridging ligands besides the μ^2(P)-coordinated bis(phosphonio)isophosphindolide moiety whose fused ring system is again orthogonal with respect to the plane through P(1), Ag(1), and Ag(2) (dihedral angle 93.7 [91.3]°). In contrast to the pronounced asymmetry of the Cu_2P unit in **3a, b**[5,6], the isophosphindole ring plane in **8** roughly bisects the Ag–P–Ag bond angle, and both Ag–P bond distances {2.393(3) [2.377(3)] and 2.419(3) [2.416(3)] Å} are very similar. Apart from this resemblance, the ligand spheres of the two metals differ significantly. In addition to the bridging P(1) atom, Ag(1) is further coordinated to a THF molecule and a weakly η^2(*O,O'*)-bonded triflate, while Ag(2) exhibits two further η^1(*O*)-bonded triflates (see Figure 2). The Ag–Ag distance {2.965(2) [2.991(13)] Å} is distinctly longer than in arylsilver compounds (Ag–Ag 2.73–2.75 Å[14]) where Ag_2C 3-centre 2-electron bonding occurs, and lies at the lower end of the range of polynuclear complexes with μ^2-(*P,P'*)-dppm [dppm = bis(diphenylphosphino)methane] bridges (Ag–Ag 2.93–3.90 Å[13,14]). If we thus neglect any bonding interactions between the metals in **8**, the geometry at Ag(2) resembles closely the planar T-shaped coordination of the silver atom in **7** (see Fig. 1b, 2b). Ag(1) can be described as having "characteristic" and "effective" coordination numbers[15] of two and four, respectively, and a distorted pseudo-tbp geometry where one of the equatorial sites is vacant and the two closest ligands occupy the axial positions. The structural parameters of the bis(phosphonio)isophosphindolide ligand show no peculiarities and are very similar to those found in **7**.

Similar coordination geometries at silver as in **7**, **8** were observed in dinuclear complexes such as [(μ^2(*P,P'*)-dppf)Ag_2(μ^2-(*O,O'*)-$PhCO_2$)$_2$][11] and [(μ^2-(*P,P'*)-dppm)-Ag_2(μ^2-(*O,O'*)-$MeCO_2$)$_2$]$_2$[12] [dppf = 1,1'-bis(diphenylphosphino)ferrocene] which both contain one bridging bisphosphane and two bridging carboxylates and where a coordination number of three at silver is enforced by the steric requirements of the ligands. A comparison of these structures with those of **7**, **8** revealed that in all cases comparable differences in the two possible Ag–O distances and P–Ag–O bond angles involving an individual silver atom occur, resulting in very similar T-shaped geometries for all metal centres. The Ag–O distances for oxygen atoms in *"trans"* position to the phosphorus atom are generally shorter (2.17–2.26 Å) than for those in *"cis"* (2.38–2.58 Å) position. In contrast, the nature of the ligand has no influence on the bond distance, and the *"trans"* Ag–O bonds in **8** are equal regardless whether the oxygen atom belongs to a THF or a triflate ligand. As compared to the

Figure 2. (a) ORTEP view (30% probability ellipsoids) of one of the two independent molecules in crystalline **8**; two of the three triflates are disordered; for the sake of clarity, only one of the two possible orientations for each of these anions is shown; (b) reduced representation of the coordination spheres of the phosphorus and silver atoms in the molecule shown in (a); O(4F) and O(4') refer to oxygen atoms in two different positions of a disordered η^1-coordinated triflate, O(1F) and O(2F) belong to a η^2-(*O,O'*) coordinated triflate anion, and O(1) denotes the oxygen of the THF ligand[a]



[a] Selected bond lengths [Å] and angles [°] (the corresponding data of the second molecule are given in brackets): Ag(1)–O(1) 2.203(8) [2.203(8)], Ag(1)–O(1F) 2.576(9) [2.674], Ag(1)–O(2F) 2.876 [2.723], Ag(1)–P(1) 2.393(3) [2.377(3)], Ag(2)–O(4') 2.15(2) [2.199(13)] Ag(2)–O(4F) 2.192(10) [2.18(2)], Ag(2)–O(7F) 2.487(9) [2.407(9)], Ag(2)–P(1) 2.419(3) [2.416(6)], P(1)–C(1) 1.742(10) [1.732(10)], P(1)–C(2) 1.741(10) [1.727(10)], O(1)–Ag(1)–P(1) 165.8(2) [166.3(2)], O(1F)–Ag(1)–P(1) 101.5(2), O(1)–Ag(1)–O(1F) 90.5(3), O(4')–Ag(2)–P(1) 151.4(9) [153.1(6)], O(4')–Ag(2)–O(7F) 99.0 [102.0(6)], P(1)–Ag(2)–O(7F) 108.7(2) [104.6(2)].

copper compounds **3a**, **b**[5,6], the more pronounced deviations from a regular trigonal geometry in **7**, **8** reflect the stronger preference of Ag^+ to adopt a linear twofold coordination. Two possible explanations may be given for the remarkable fact that the THF ligands in **7**, **8** always occupy the "*trans*" position and thus exhibit stronger Ag−O bonds than the triflate anions at the same metal, viz. (i) the known nucleofugacity of the triflate anion, and (ii) electrostatic attraction between the negatively polarised triflate and the adjacent positively charged PPh_3 group.

NMR-Spectroscopic Investigations in Solution

The ^{31}P-NMR spectra obtained after dissolution of the pure silver complexes in CH_2Cl_2 (**4a**, **5a**) or THF (**7**, **8**) were identical with those of the crude reaction mixtures. Apparently, all complexes undergo partial dissociation to form a dynamic equilibrium involving mono- and disilver complexes as well as the free ligand. Unambiguous identification of the individual species was nonetheless possible on the basis of ^{31}P-NMR spectra recorded at temperatures between −50 and −120 °C under slow exchange conditions (Table 1). **4a** and **5a** as well as the dinuclear complex **9** were further characterised by their ^{109}Ag-NMR data which were obtained from ^{31}P detected heteronuclear $^{31}P,^{109}Ag$ shift correlations[16]

Table 1. ^{31}P- and ^{109}Ag-NMR data of the silver complexes **4**, **5**, **7−11** in solution

		T [°C]	$\delta^{31}P$ >P-Ag [ppm]	$\delta^{31}P$ -PPh_3 [ppm]	$^2J_{PP}$ [Hz]	$\delta^{109}Ag$ [ppm]	$^1J_{^{109}Ag,^{31}P}$ [Hz]
7[a]	(1)Ag(OTf)(thf) [c]	-50	187.3	13.7	77.3	528.5	825 [d]
8[a]	(1)$Ag_2(OTf)_3$(thf)	-110	102.9	11.8	69	-	492 [e]
4a[b]	(1)$Ag(OTf)_2$	-50	188.5	13.7	77.3	502.1	831.6 [f]
4b[b]	(6)$Ag(OTf)_2$	-100	193.3	9.5	79	-	808
5a[b]	$[(1)Ag_2(OTf)_2]^+$ [g]	-120	98.8	10.6	70.4	-	520 [e]
5b[b]	$[(6)Ag_2(OTf)_2]^+$ [g]	-100	104.7	8.1	70.5	-	519
9[b]	$(1)Ag_2(\mu\text{-}CF_3CO_2)]^{2+}$ [g]	-70	131.0	12.3	73.8	764.3	440
10[b]	$[(6)Ag]^{2+}$ [g]	-100	193.5	9.5	81.4	-	749 [e]
11[b]	$[(6)Ag_2(\mu\text{-}CF_3CO_2)]^{2+}$ [g]	-100	140.8	8.6	73.8	-	441

[a] In THF. − [b] In CH_2Cl_2. − [c] OTf = $CF_3SO_3^-$. − [d] $^3J_{Ag,P}$ = 1.4 Hz. − [e] The value for $^1J_{^{109}Ag,^{31}P}$ was calculated from the observed average coupling constant 0.5 ($^1J_{^{109}Ag,^{31}P}$ + $^1J_{^{107}Ag,^{31}P}$). − [f] $^3J_{Ag,P}$ = 2 Hz. − [g] The presence of additional ligands and coordination number three at silver is likely; the ligands are omitted in the formula since their character and number could not be determined from the NMR data.

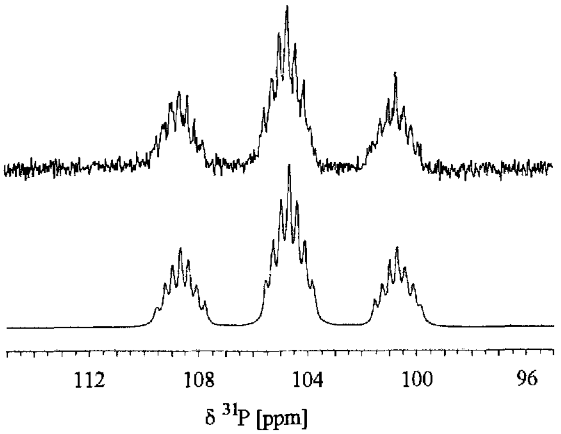
The ^{31}P-NMR signals of the mononuclear complexes **4a**, **b** and **7** appeared as well resolved multiplets and can be described as the superposition of two AM_2X spectra [X denotes the two isotopes ^{107}Ag (I = 1/2, 51.82% nat. abundance) and ^{109}Ag (I = 1/2, 48.18%)]. The values of $^1J_{^{109}Ag,^{31}P}$ are comparable to those of phosphane complexes of the type $(R_3P)AgX$ (X = nonphosphorus-containing ligand, $^1J_{^{109}Ag,^{31}P}$ = 750−880 Hz[17,18]) and indicate a σ-coordination of the cationic ligand via the phosphorus lone pair, in accord with the crystal structure of **7**. The magnitude of the $^2J_{PP}$ couplings is smaller than in uncoordinated **1** and **6**. Analysis of the observed signal multiplicities proved the absence of higher order splittings, suggesting that no oligomers were formed in solution. Even if the number and nature of additional ligands at the metals could not be directly derived from the observed ^{31}P- and ^{109}Ag-NMR data, further indications were obtained from the comparison of solid-state and solution NMR data. The values for $\delta^{31}P$ and $^1J_{^{109}Ag,^{31}P}$ in **4a**, **b** and **7** are all quite similar and compare closely with the corresponding solid-state data of **4a**, suggesting that a coordination number of three at silver which was established from the crystal structure determination of **7** holds true in all cases. The small but distinct differences between the solution NMR data of **4a** and **7** may be attributed to differences in the ligand spheres. If we assume in both cases the presence of one coordinated triflate in addition to the cation **1** because of electrostatic reasons, we may deduce that the third coordination site is occupied either by a THF molecule or, in non-coordinating solvents (CH_2Cl_2, $CHCl_3$), by the second triflate anion. This hypothesis was further corroborated by the fact that identical ^{31}P- and ^{109}Ag-NMR parameters as for **7** were detected after 10% of THF had been added to a solution of **4a** in CH_2Cl_2; the observed changes suggest that a ligand displacement with concomitant transformation of **4a** into **7** had occurred.

The signals of the metal-bonded phosphorus nuclei in the disilver complexes **5a** and **8** appeared as broad triplets due to the coupling with two adjacent metal nuclei which allowed only the determination of an average value for $^1J_{^{107/109}Ag,^{31}P}$. While $^2J_{PP}$ was obtained from the splitting of the PPh_3 resonance, short effective relaxation times prevented the measurement of ^{109}Ag chemical shifts. **5b** displayed narrower lines permitting the resolution of the individual subspectra of the three different isotopomers and the extraction of all relevant couplings by means of spectral simulations (see Figure 3). As compared with **4a**, **b** and **7**, the resonance of the μ^2-bridging phosphorus in **5a**, **b** and **8** exhibits increased coordination shifts and a reduced magnitude of $^1J_{^{109}Ag,^{31}P}$. Both effects can be explained as a consequence of the higher coordination number at phosphorus. In the case of **8**, the observed line-broadening effects are rationalised by the conjecture of a mutual exchange of the THF and triflate ligands, leading to dynamic averaging of the two distinguishable silver environments. For **5a**, coordinative saturation of the metals could be achieved by oligomerisation of the cations and anions shown in Scheme 3.

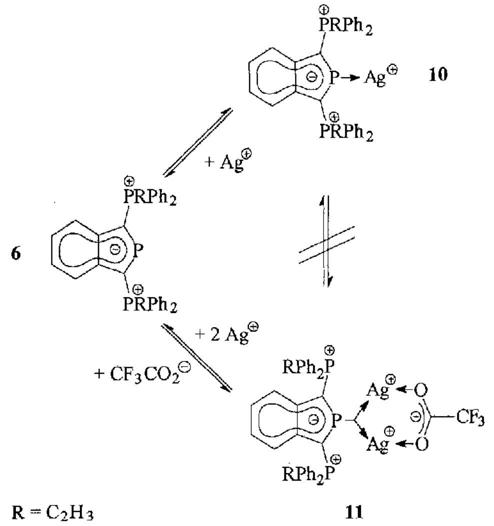
The ^{31}P-NMR data of the dinuclear complexes formed in the reactions of CF_3CO_2Ag with the cations **1** and **6** (**9**, **11** in Table 1) exhibit some notable differences as compared to those of **5a**, **b** and **8**: (i) $\delta^{31}P$ of the metal-bonded phosphorus is shifted by approx. 30 ppm to lower field and adopts similar values as in the copper complexes **3**[5]; (ii) $^1J_{^{109}Ag,^{31}P}$ is smaller by approx. 60 Hz; (iii) only small amounts of mononuclear complexes (**10**) were observed besides the dinuclear species, even in the presence of a large excess of the free cations **1**, **6**; (iv) the longer effective transversal relaxation rates of the resonance of the metal bonded phosphorus permitted to obtain $\delta^{109}Ag$ of **9** from a $^{31}P,^{109}Ag$ shift correlation.

In particular the two latter aspects clearly indicate that **9**, **11** are both kinetically and energetically more stable than **5a** and **8**. On the basis of the results of ^{31}P-NMR investigations of the equilibrium mixture obtained from the reaction of **6**[Cl] with an excess of CF_3CO_2Ag, it is suggested that this higher stability results from the presence of extra μ^2-(*O,O'*)-trifluoroacetate ligands in addition to the μ^2-bridging isophosphindolium cation. The conventional $^{31}P\{^1H\}$-NMR spectrum (−80 °C, CH_2Cl_2) of the studied solution displayed besides the signals of **7** the resonances of two silver complexes which were readily assigned as the mono- and dinuclear complexes **10**, **11** (Scheme 4 and Figure 4). $^{31}P,^{31}P$ EXSY spectra obtained at the same temperature and with mixing times between 250 and 950 ms displayed cross-peaks which indicated that dynamic interconversion of **6** with either of the two complexes takes place; in contrast, a correlation signal pointing to a direct interconversion between **10** and **11** was not observed (Figure 4). If **11** contained only a single μ^2-bridging isophosphindolide ligand, any rupture of an Ag−P bond would necessarily lead to its direct transformation into the mononuclear complex **10**, in contradiction to the experimental results. On the other hand, if a second bridging ligand was present, dissociation would occur only after cleavage of two bonds. Since cleavage of one Ag−P and one Ag−O bond would equally result in a direct interconversion **11** → **10**, the dissociation of **11** must occur via cleavage of both Ag−P bonds, yielding **6** together with a dinuclear silver complex which evades detection by ^{31}P-NMR spectroscopy (it can be speculated that a species containing a $(\mu^2\text{-}CF_3CO_2)_2Ag_2$ unit with a similar constitution as in solid CF_3CO_2Ag[19] is formed). Formation of the mononuclear complex **10** would be achieved in a subsequent reaction between this product and the cation **6**, leading to the overall reaction scheme depicted in Scheme 4. Despite the strong evidence for the presence of a cyclic structure of **11**, further elucidation of the ligand sphere at silver was not feasible. The comparison of the $\delta^{109}Ag$ and $^1J_{^{109}Ag,^{31}P}$ values with those of **5** and **8** suggested the presence of three-coordinate silver atoms; however, even if this assumption is correct, it cannot be decided if another μ^2-bridging or, alternatively, two terminal trifluoroacetate moieties are present.

Figure 3. (a) Expansion of the signal of the metal-bonded phosphorus in the $^{31}P\{^1H\}$-NMR spectrum of **5b** (−90 °C, CH_2Cl_2); (b) result of a fit of the intensity-weighted superposition of the subspectra of individual isotopomers to the experimental spectrum by using the programme WINDAISY; final parameters for the fit were $\delta^{31}P = 104.67$, $^1J_{^{109}Ag,^{31}P} = 519$ Hz, $^1J_{^{107}Ag,^{31}P} = 449$ Hz, $^2J_{PP} = 70.1$ Hz



Scheme 4. Schematic presentation of the equilibria observed in the reaction of cation **6** with CF_3CO_2Ag; with the exception of the bridging trifluoroacetate in **11**, additional ligands at silver are omitted



Discussion

The observed reactivities of bis(phosphonio)isophosphindolide salts L[X] (L = **1**, **6**, $X^- = Cl^-$, $CF_3SO_3^-$, $CF_3CO_2^-$) towards silver salts AgY ($Y^- = CF_3SO_3^-$, $CF_3CO_2^-$, $CH_3CO_2^-$, 1/2 SO_4^{2-}) revealed that the outcome of the reaction depends subtly on the relative nucleophilicities of the cations L and the available counterions, X and Y, towards the Lewis acid, Ag^+. Quantitative complexation of L was observed only in the presence of strongly nucleofugic triflate anions. The less nucleofugic trifluoroacetate successfully competes with L for the Lewis acid centre; coordination of L to the metal is observed, but remains incomplete. The acetate and sulfate anions apparently form much stronger bonds to Ag^+ and complexation of L is negligible or not observed at all in the presence of these ligands. Likewise, the stability constants of the spectroscopically detected silver complexes of L are too low to prevent precipitation of sparingly soluble silver halides. Since stable and soluble complexes of silver halides with donors such as tertiary amines and phosphanes[17,18] are well known, the cations **1** and **6** are apparently much weaker donors towards Ag^+ than tertiary phosphanes or amines. The same sequence of relative donor strengths was observed for complexes of Au(I)[4].

All bis(phosphonio)isophosphindolide silver complexes described in this study exhibit ligand-to-metal (L/Ag) ratios of either 1:2 or 1:1, referring to compositions of "LAg" and "LAg_2". The formation of complexes with higher L/Ag ratios, which is quite common even for sterically demanding phosphanes[18,20], was not observed. As in the case of the

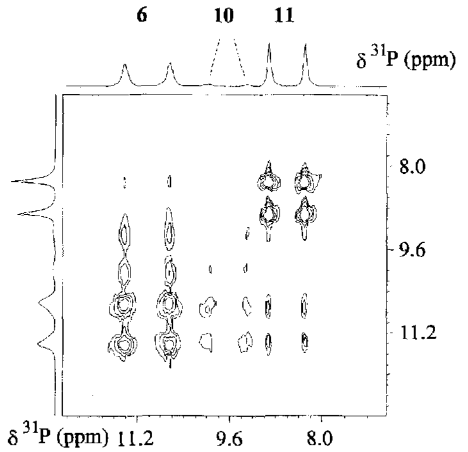


Figure 4. Expansion of the phosphonio region in the ^{31}P,^{31}P EXSY spectrum (−80 °C, CH_2Cl_2, mixing time 450 ms) of a solution obtained from reaction of equimolar amounts of **6**[CF_3SO_3] and CF_3CO_2Ag; the 1D projections on the top and left sides were obtained from a conventional $^{31}P\{^1H\}$-NMR spectrum; the assignment of the signals is given in the top trace

copper complexes **3a**, **b**[5,6], the reason for this reluctance as well as for the enforcement of a low coordination number and a planar geometry at the metal can be attributed to the high degree of steric shielding which results from the encapsulation of the metal centre between the phosphonio groups of L. The influence of the anion on the relative stabilities of LAg and LAg_2 is clearly documented by the different composition of the equilibrium mixtures obtained in the reactions of **1**[X] with AgX ($X^- = CF_3SO_3^-$, $CF_3CO_2^-$). This suggests that the mononuclear complex is somewhat more stable than the dinuclear complex for $X^- = CF_3SO_3^-$, while the reverse is true for $X^- = CF_3CO_2^-$. Even if the different nucleophilicities of X certainly contribute to this effect, it may readily be assumed that the major driving force are the presence of an additional bridging ligand and the concomitant formation of a cyclic structure in the dinuclear trifluoroacetato complexes.

The bonding of the ligand **1** to one and two metal atoms in the complexes **7** and **8** may be compared with the known types of coordination modes for bis(phosphonio)isophosphindolide cations in **2**[4] and **3**[5,6]. Whereas the planar coordination of the metal-bonded phosphorus and the rather short Ag−P distance in **7** are in accord with a classification as a terminal phosphenium complex similar to **2**[3], the structural features of **8** raise the question if the bonding in the Ag_2P unit should be described in terms of an electron-deficient 3-centre bond as in **3**[5,6], or rather as two electron-precise single bonds as in μ^2-phospholyl complexes[8]. The second model is favoured by the observations that, in contrast to **3**, both Ag−P bond lengths lie in the range of normal bonds lengths of comparable phosphane complexes[11−14] and that the larger Ag−Ag distance suggests that Ag−Ag bonding interactions are of minor importance. On the other hand, since the ligand would then act as a 4-electron donor, a notable lengthening of the endocyclic P−C bonds should be expected[8], which was in fact not observed. For a further elucidation of this aspect, a comparison of the bonding situation in **8** with complexes containing heterocyclic phosphorus-pπ-systems in a related coordination mode is useful. Schmid et al. recently reported the complex $[Ir_2(1,5\text{-cod})_2(\text{niphos})_2][SbF_6]_2$ [niphos = 2-(2-pyridyl)phosphinine] where the iridium centres are bridged by two μ^2(P)-coordinated phosphinine fragments and the structural parameters in the Ir_2P_2 unit closely resemble those of related μ^2-phosphide complexes[21]. Based on the observation that the bond lengths in the niphos ligand in this compound do not differ significantly from those of complexes exhibiting the same ligand in a terminal, η^1(P)-coordination mode, Schmid et al. concluded, however, that the phosphinine should still be considered as a 2-electron donor[21]. In the light of these findings, the equivalence of the structural parameters of the bis(phosphonio)isophosphindolide ligands in **3** and **8** and the similarity of the electronic spectra of both complexes suggest that the bonding in the Ag_2P fragment in **8** should be described as in the case of **3**[5,6] as a 3-centre 2-electron bond. However, even if the dominant contribution to the bonding may still arise from the P(σ)→Ag electron transfer, the shorter phosphorus-metal and longer metal-metal distances in **8** can be taken as an indication that the P(π)→Ag and Ag→P(π*) interactions, which possess metal-metal antibonding character, gain increasing importance.

In conclusion, the suitability of bis(phosphonio)isophosphindolide cations to act as ligands towards coinage metals was further confirmed. The Ag−P bonds in the formed complexes appear to be rather weak, resulting in partial dissociation and formation of dynamic equilibria in solution. Nevertheless, the cations may bind in a μ^2,η^1 fashion to two metals, suggesting that the contribution of the highly polarisable π-electron system to metal−ligand bonding is of equal importance as the nucleophilicity of the phosphorus lone pair. The observed formation of **8** indicates that dinuclear complexes with μ^2,η^1-coordinated cations may be realised even in the absence of further bridging ligands; however, NMR spectroscopic studies furnish evidence that the disposition to form dimetallic species is greatly enhanced by such ligands.

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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**[Br][1], **1**[CF_3SO_3][4], and **6**[Br][2] was described elsewhere. **6**[CF_3SO_3] was prepared in analogy to the procedure given for **1**[CF_3SO_3][4] (m.p. 235 °C, ^{31}P- and ^{1}H-NMR spectra identical with those of **6**[Br]). − Solution NMR spectra: Bruker AMX 300 (^{31}P: 121.5 MHz; ^{109}Ag: 13.97 MHz). ^{109}Ag chemical shifts were determined from ^{31}P detected ^{31}P,^{109}Ag HMQC spectra[16]. Solid-state ^{31}P-NMR spectra: Varian Unity 400 (^{31}P: 161.90 MHz) under MAS conditions and high-power proton decoupling. All chemical shifts are referenced to external 85% H_3PO_4 and Ag^+_∞ (Ξ =

4.653623 MHz); a positive sign denotes a shift to lower frequencies. Coupling constants are given as absolute values, heteronuclear couplings between phosphorus and silver nuclei are given as $^{1}J_{^{109}\mathrm{Ag},^{31}\mathrm{P}}$ if not mentioned otherwise. Solvent contents of isolated compounds were determined by integration of suitable ^{1}H-NMR resonances. – MS: Kratos Concept 1 H, Xe-FAB, *m*-NBA matrix; molecular masses refer to the most abundant isotopes. – UV-Vis remission spectra: Cary 2400, powdered solid samples were mixed with $BaSO_4$. – Melting points were determined in sealed capillaries. – Elemental analyses: Heraeus CHNO-Rapid.

General Procedure for the Reaction of Bis(phosphonio)isophosphindolide Salts with AgY (Y⁻ = $CF_3SO_3^-$, $CF_3CO_2^-$, $CH_3CO_2^-$, 1/2 SO_4^{2-}: (a) A mixture of 1 mmol of the bis(phosphonio)isophopshindolide salt (**1**[X], **6**[X], X⁻ = $CF_3SO_3^-$, Br^-) and the appropriate amount of silver salt AgY (Y⁻ = $CF_3^-SO_3^-$, $CH_3CO_2^-$) was treated with 5 ml of CH_2Cl_2. The formed mixture was stirred for 10 min during which time most or all of the solids dissolved. Any residual solids were decanted off, and the supernatant solutions were analyzed by NMR spectroscopy. ^{31}P-NMR spectra obtained from the reaction of equimolar amounts of (**1**, **6**)[Br] and AgY were identical with those of the reactants. The ^{31}P- and ^{109}Ag-NMR data of the detected complexes **4**, **5** are collected in Table 1.

(b) A mixture of 1 mmol of **1**[Br] or **6**[Br] and 2 or 3 mmol of CF_3CO_2Ag was treated with 10 ml of CH_2Cl_2 and stirred for 10 min. The formed dark red suspension was filtered and the filtrate analyzed by NMR spectroscopy. The NMR data of the detected complexes **9**–**11** are collected in Table 1. In the reaction of **1**[Br], also trace amounts of a mononuclear complex were detected in addition to **9**, however, a secure identification was impeded by the insufficient signal-to-noise ratio. The solutions were found to decompose within a few hours with formation of a silver mirror as well as red, intractable solid which could not be identified.

(c) A mixture of 1 mmol of **1**[CF_3SO_3] and 1 mmol of Ag_2SO_4 was treated with 5 ml of CH_2Cl_2. After stirring for 5 min, enough methanol was added to afford complete dissolution of all solids. ^{31}P-NMR spectra of the resulting solution were found to be identical with those of pure **1**[CF_3SO_3] at temperatures between 25 °C and −60 °C.

Silver Complexes

4a: 100 mg (0.39 mmol) of CF_3SO_3Ag and 313 mg (0.39 mmol) of **1**[CF_3SO_3] were each dissolved in 10 ml of $CHCl_3$. The solutions were combined and stirred for 1 h. The resulting, bright yellow solution was concentrated in vacuo to a volume of 6 ml and stored for several days at −25 °C. The separated crystals of **4a** were collected by filtration and dried in a stream of argon. The product was characterised by its ^{31}P- and ^{109}Ag-NMR spectra (Table 1). An ^{1}H-NMR spectroscopic assay revealed the presence of 2 to 2.25 equivalents of $CHCl_3$ per formula unit. Because of rapid degradation of the crystals which was accompanied by partial loss of the included solvent, no satisfactory elemental analysis was obtained. Yield: 135 mg (25%); m.p. >172 °C (dec.).

5a: 200 mg (0.78 mmol) of CF_3SO_3Ag and 313 mg (0.39 mmol) of **1**[CF_3SO_3] were each dissolved in 10 ml of $CHCl_3$. After stirring of the combined solutions for 1 h a yellow solution and a yellow microcrystalline precipitate had formed. The mixture was warmed gently to dissolve as much of the solid as possible and filtered hot. The clear yellow filtrate was kept for several days at +7 °C. The separated yellow crystalline product was collected by filtration and dried in a stream of argon. Because of degradation of the crystals accompanied with loss of $CHCl_3$, no satisfactory elemental analysis was obtained. In addition to characterisation by solid-state ^{31}P-NMR spectroscopy, a single crystal was studied by X-ray diffractometry. Even it a final structure solution was prevented by massive absorption effects and the fact that the severe disorder present in part of the structure could not be satisfactorily resolved, the available data confirmed the proposed composition [(μ^2-**1**)$Ag_2(OSO_2CF_3)_2$][SO_3CF_3] · 3 $CHCl_3$. The presence of three equivalents of solvent per formula unit was confirmed by ^{1}H-NMR spectroscopy. Yield: 125 mg (19%); m.p. >232 °C (dec.). – ^{31}P{^{1}H} NMR (solid): δ = 95.2 (t, $J_{\mathrm{Ag,P}}$ = 473 Hz, Ag_2P), 13.3 (PPh_3). – Solution ^{31}P-NMR data are given in Table 1. – (+)-FAB-MS; *m*/*z* (%): 1171 (2) [$C_{46}H_{34}Ag_2F_6O_6P_3S_2^+$]; 1066 (6) [$C_{45}H_{34}AgF_3O_3P_3S^+$ + matrix]; 913(8) [$C_{45}H_{34}AgF_3O_3P_3S^+$], 655 (100) [$C_{44}H_{34}P_3^+$].

7: A solution of 316 mg (1.23 mmol) of CF_3SO_3Ag in 10 ml of THF was added to a suspension of 1.10 g (1.23 mmol) of **1**[CF_3SO_3] in 20 ml THF. The resulting clear solution was stirred for 1 h and then concentrated in vacuo until the complex began to precipitate. The formed solid was redissolved by gentle warming, and the resulting solution kept at +7 °C for several weeks. **7** crystallised as colourless prisms which were collected by filtration and dried in a stream of dry argon. Yield 1.20 g (76%); m.p. >130 °C (dec.). – ^{31}P{^{1}H} NMR (solid): δ = 201.4 (d, $J_{\mathrm{Ag,P}}$ = 805 Hz, AgP), 15.7 (PPh_3). – Solution ^{31}P{^{1}H}- and ^{109}Ag-NMR data are given in Table 1. – UV ($BaSO_4$): λ_{max} = 341 (sh), 357 nm. – (+)-FAB-MS; *m*/*z* (%): 913 (4) [$C_{49}H_{42}AgF_3O_4P_3S^+$ – THF], 655 (100) [$C_{44}H_{34}P_3^+$]. – $C_{58}H_{58}AgF_6O_9P_3S_2$ (1277.99): calcd. C 54.51, H 4.58; found C 54.58, H 4.59.

8: A solution of 200 mg (0.78 mmol) of CF_3SO_3Ag in 5 ml of THF was added to a suspension of 310 mg (0.39 mmol) of **1**[CF_3SO_3] in 5 ml of THF. After stirring for 1 h, the resulting intensively yellow solution was cooled to −25 °C and stored at this temperature for several days. The separated crystalline product was collected by filtration and dried in a stream of argon. The dry crystals turned rapidly cloudy due to partial loss of the contained solvent, thus preventing to obtain a satisfactory elemental analysis. ^{31}P-NMR spectroscopic investigations indicated, however, that no further decomposition had occurred. Yield: 410 mg (60%); m.p. >225 °C (dec.). – ^{31}P{^{1}H} NMR (solid): δ = 106.3 (t, $J_{\mathrm{Ag,P}}$ = 514 Hz) and 100.9 (t, $J_{\mathrm{Ag,P}}$ = 514 Hz) (AgP), 11.8 (d, J_{PP} = 72 Hz) and 11.4 (d, J_{PP} = 72 Hz) (PPh_3). – Solution ^{31}P{^{1}H}-NMR data are given in Table 1. – UV ($BaSO_4$): λ_{max} = 359, 409 (sh) nm. – (+)-FAB-MS; *m*/*z* (%): 1066 (0.4) [$C_{49}H_{42}AgF_3O_4P_3S^+$ – THF + matrix], 913 (10) [$C_{49}H_{42}AgF_3O_4P_3S^+$ – THF], 655 (100) [$C_{44}H_{34}P_3^+$].

Crystal-Structure Determination of **7** *at 200(2) K:* Colourless prisms, [$C_{50}H_{42}AgF_6O_7P_3S_2$] · 2 THF, *M* = 1277.9, crystal size 0.28 × 0.25 × 0.10 mm, monoclinic, space group *C*2/*c* (No. 15): *a* = 21.091(2), *b* = 20.277(2), *c* = 13.479(1) Å, β = 92.99(1)°, *V* = 5756.5(8) Å^3, *Z* = 4, $\rho_{\mathrm{calcd.}}$ = 1.475 Mg m^{-3}, *F*(000) = 2624, μ(Cu-K_α) = 4.92 mm^{-1}. 4491 reflections (4273 independent reflections with R_{int} = 0.037) were collected on a Enraf-Nonius CAD4 diffractometer (Cu-K_α radiation, graphite monochromator, 2θ/ω scans) in the range $5 \leq 2\Theta \leq 140°$ ($-23 \leq h \leq 23$, $-2 \leq k \leq 22$, $-15 \leq l \leq 6$). Of these, 4272 were used for structure solution (direct methods) and refinement (full-matrix least squares on F^2, 416 parameters and 108 restraints, non hydrogen atoms anisotropic, hydrogens with a "riding" model); wR_2 = 0.135 {R_1 [$I > 2\sigma(I)$] = 0.046}. An empirical absorption correction with the programme DIFABS[22] was applied. The THF and the bis(triphenylphosphonio)isophosphindolide cation occupy a special position on the crystallographic C_2 axis. The silver and the triflate anion are disordered.

Crystal-Structure Determination of **8** *at 153(2) K:* Yellow plates, [$C_{51}H_{42}Ag_2F_9O_{10}P_3S_3$] · 5 THF, *M* = 1751.2, crystal size 0.4 × 0.3

× 0.20 mm, triclinic, space group $P\bar{1}$ (No. 2): $a = 18.103(3)$, $b = 18.908(3)$, $c = 22.344(4)$ Å, $\alpha = 90.53(2)$, $\beta = 90.13(2)$, $\gamma = 93.33(2)°$, $V = 7635(2)$ Å^3, $Z = 4$, $\rho_{calcd.} = 1.523$ Mg m^{-3}, $F(000) = 3584$, $\mu(\text{Mo-}K_\alpha) = 0.74$ mm^{-1}. 20275 reflections were collected on a STOE AED diffractometer (Mo-K_a radiation, graphite monochromator) of an oil coated, rapidly cooled crystal[23] in the range $8 \leq 2\Theta \leq 45°$ ($-19 \leq h \leq 19$, $-20 \leq k \leq 20$, $-9 \leq l \leq 24$). 19838 independent reflections ($R_{int} = 0.042$) were used for the solution (direct methods[24]) and refinement (full-matrix least squares[25] on F^2, 2187 parameters and 4605 restraints, non-hydrogen atoms anisotropic, hydrogens with a "riding" model); $wR_2 = 0.242$ $\{R_1\ [I > 2\sigma(I)] = 0.086\}$. A semiempirical absorption correction from Ψ-scans was applied (max. and min. transmission 0.824 and 0.732). Four of the six triflate anions and three of ten THF molecules were disordered.

Further details of the crystal structure investigations are available on request from the Director of the Cambridge Crystallographic Data Centre, 12 Union Road, GB-Cambridge CB2 1EZ, on quoting the complete journal citation.

☆ Dedicated to Professor Dr. *Rolf Appel* on the occasion of his 75th birthday.

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