“Preparation of Stable $AsBr_4^+$ and $I_2As\text{-}PI_3^+$ Salts. Why didn’t we Succeed to Prepare AsI_4^+ and $As_2X_5^+$? A Combined Experimental and Theoretical Study.”

by

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Supplemental to the Experimental Section

Reactions between 1-2 equivalents of $AsBr_3$ and $Ag[Al(OR)_4]$

Reaction 1 (in the solution of CH_2Cl_2): $Ag[Al(OR)_4]$ (0.497 g, 0.428 mmol) in 10 ml of CH_2Cl_2 was placed into a two bulbed vessel closed with *Young*-valves. The solvent was evaporated in vacuum until the weight of the flask was constant. $AsBr_3$ (0.269 g, 0.856 mmol) was added to the silver salt followed by cooling the flask to –78°C. CH_2Cl_2 (10 ml) was poured into the other bulb of the flask and condensed onto the reaction mixture at –78°C. No reaction was observed in the range from –78°C to –30°C. When storing the flask at –30°C off-white solids precipitated (AgBr). The solution was filtered and concentrated to about 2-3 ml. From the dark brown solution were obtained only the crystals of $AsBr_3$ (unit cell determination). All the volatiles were removed in vacuuo and the flask was weighed (0.190 g residual solids) indicating substantial anion decomposition. No defined product could be extracted.

Reaction 2 (in CH_2Cl_2/CS_2 solution): $Ag[Al(OR)_4]$ (0.227 g, 0.196 mmol) was weighed into a flask connected through a frit plate with a NMR tube glass-blown into it. $AsBr_3$ (0.062 g, 0.196 mmol) was loaded into the reaction flask followed by cooling to –78°C. CS_2 (2 ml) and CH_2Cl_2 (4 ml) were added in a sequence and flask was occasionally shaken. After about 30 minutes all the volatiles were evaporated until no weight change was observed. The residue (yellowish solids, 0.164 g, indicative of anion decomposition) was extracted with CD_2Cl_2 directly into the NMR tube. The sample gave only very weak signals both in ^{27}Al NMR and in ^{13}C NMR only two middle signals of the quartet of CF_3 was observed: ^{13}C NMR (63 MHz, CD_2Cl_2, –30°C): δ = 120.3 (q, J_{CF} = 292.4 Hz, CF_3); ^{27}Al NMR (78 MHz, CD_2Cl_2, –30°C): δ = 37.4 (s, $\nu_{1/2}$ = 20 Hz)

Reaction 3 (in the solid state): Ag[Al(OR)$_4$] (1.077 g, 0.862 mmol) and $AsBr_3$ (0.588 g, 1.724 mmol) were transfered into a two bulbed vessel under argon atmosphere. The mixture was kept at room temperature. The reaction started immediately after mixing the starting materials (occasionally shaken) resulting in a softening of the mixture simultaneously with changing of the color. The slightly brown mixture became liquid for a short time and than solidified again with precipitation of AgBr. The resulting mixture was extracted few times with pentane and concentrated. Thereby crystals of $AsBr_3$ formed. After removal of all volatiles from the extract a white residue remained, that got dark within a few minutes. After removing all volatiles the residue weighted 0.836 g (loss of weight 49%). The residue was dissolved in the 3:1 CH_2Cl_2/THF and stored at –30°C. Colorless crystals of $[(RO)_2AlF(THF)]_2$ were grown from this solution and isolated (0.473 g, 88 % yield calculated for Ag[Al(OR)$_4$]).

^{1}H NMR (250 MHz, CD_2Cl_2, +25°C): δ = 4.28 (m, O–CH_2, THF), 2.13 (m, CH_2, THF);
^{13}C NMR (63 MHz, CD_2Cl_2, +25°C): δ = 121.1 (q, J_{CF} = 290.8 Hz, CF_3), 74.5 (s, –OCH_2–, THF), 73.7 (s, OCH_2, THF), 25.5 (s, CH_2, THF), 25.3 (s, CH_2, THF).

Reactions between 1-2 equivalents of AsI$_3$ and Ag[Al(OR)$_4$]

Reaction 1 (in the NMR tube): Ag[Al(OR)$_4$] (0.115 g, 0.099 mmol) was placed into a NMR tube glass-blown onto a valve followed by 1 ml of CD_2Cl_2. The NMR tube was cooled to –78°C and AsI_3 (0.090 g, 0.198 mmol) was added. The sample was kept initially at –78°C and occasionally shaken but the most of AsI_3 remained still not dissolved. If the sample was immediately cooled after warming the precipitation of yellow solids were observed, that could be reversibly dissolve after rising the temperature in a short time. When the cooling process was carried out slowly the characteristic crystals of AsI_3 were formed rather than yellow precipitates. The sample was stored at different temperatures for different periods of time (1 day at –78°C, 1 week at –30°C and 1 month at RT) and was checked by ^{27}Al and ^{13}C NMR spectroscopy. No AgI precipitation was observed and the NMR of the intact anion remained unchanged. The sample was exposed to UV radiation at –30°C. After a month at RT (sample was exposed to the sunlight) a little decomposition product was found in the ^{13}C NMR but to our surprise still no precipitation of AgI was observed.

(The sample stored at –78°C) ^{13}C NMR (63 MHz, CD_2Cl_2, –40°C): δ = 120.8 (q, J_{CF} = 292.5 Hz, CF_3 of the $[Al(OR)_4]^-$ anion), 78.0 (broad, $C(CF_3)_3$); ^{27}Al NMR (78 MHz, CD_2Cl_2, –30°C): δ = 37.7 (s, $\nu_{1/2}$ = 15 Hz)

(The sample exposed to UV light and stored at –30°C) ^{13}C NMR (63 MHz, CD_2Cl_2, –30°C): δ = 120.9 (q, J_{CF} = 292.6 Hz, CF_3 of the $[Al(OR)_4]^-$ anion), ^{27}Al NMR (78 MHz, CD_2Cl_2, 25°C): δ = 78.6 (broad, $C(CF_3)_3$)

(The sample stored about one month at RT) ^{13}C NMR (63 MHz, CD_2Cl_2, –40°C): δ = 120.9 (q, J_{CF} = 292.0 Hz, CF_3 of the $[Al(OR)_4]^-$ anion), in low intensity: 120.4 (q, J_{CF} = 291.1 Hz, CF_3), 119.9 (q, J_{CF} = 292.3 Hz, CF_3); ^{27}Al NMR (78 MHz, CD_2Cl_2, –30°C): δ = 36.7 (s, $\nu_{1/2}$ = 10 Hz), δ_{range} = 70 - 0 (broad, $\nu_{1/2}$ = 2560 Hz).

Reaction 2 (in CH_2Cl_2/CS_2 solution): $Ag[Al(OR)_4]$ (0.319 g, 0.275 mmol), AsI_3 (0.251 g, 0.550 mmol) were placed into a two bulbed vessel. CS_2 (3 ml) and CH_2Cl_2 (8 ml) were condensed onto the mixture in a sequence at –78°C and flask was occasionally shaken. After about 30 minutes the flask was allowed to warm to –30°C and was magnetically stirred at this temperature for 3 hours. During this procedure the reaction mixture was occasionally warmed to ambient temperature and following observation were made: yellow solids (AsI_3) precipitated reversibly from the warm solution immediately after recooling to –30°C. If the flask was cooled very slowly, AsI_3 crystals (X-Ray, cell determination) were obtained exclusively. No AgI precipitation was observed. After usual work-up all the volatiles were evaporated and the flask was weighted (0.580 g of the residual solids). Unlike in the reaction between $AsBr_3$ and $Ag[Al(OR)_4]$ **no anion decomposition** was observed according to the mass balance.

Reaction 3 (in the solid state): Freshly prepared, solvent free, $Ag[Al(OR)_4]$ (0.098g, 0.091 mmol) and AsI_3 (0.077 g, 0.182 mmol) were weighted into mortar under Ar atmosphere (in the glove box). The mixture had slightly yellow color (AsI_3 color). It was ground intensely about 20 minutes and after the end of this procedure the mixture was colored much more intensive (deeply orange color) than at the beginning. An IR sample in Nujol was prepared and compared with spectra of solvent free $Ag[Al(OR)]_4$ from the same batch and $Ag(CH_2Cl_2)_3^+[Al(OR)_4]$. Since the spectrum of the solid reaction mixture did not resemble that of the solvent free $Ag[Al(OR)_4]$, but was very similar to the $Ag(CH_2Cl_2)_3^+[Al(OR)_4]$ spectrum, we propose the coordination of the AsI_3 to the silver cation and formation of the complex $Ag(AsI_3)_x^+[Al(OR)_4]$. The stoichiometry and constitution of the complex, however, could not be deduced from this spectrum since no vibrations, that could be tentatively assigned to the $Ag(AsI_3)_x^+$ complex, were observed.

Reactions between $AsBr_3$, P_4 and $Ag[Al(OR)_4]$

Reaction in the NMR tube: $Ag[Al(OR)_4]$ (0.138 g, 0.128 mmol), P_4 (0.018 g, 0.128 mmol) and $AsBr_3$ (0.041 g, 0.128 mmol) were placed into a NMR tube glass-blown onto a valve. The tube was cooled to –78°C and CD_2Cl_2 (1 ml) was added. The sample was closed and shaken from time to time untill the off-white solids (AgBr) precipitated. The reaction was stored at -28°C (5 days) before the NMR spectra were recorded.

^{13}C NMR (63 MHz, CD_2Cl_2, –50°C): δ = 121.0 (q, J_{CF} = 291.0 Hz, CF_3 of the $[Al(OR)_4]^-$ anion), 121.5 (q, J_{CF} = 292.4 Hz, CF_3 of the decomposition product); ^{31}P-NMR (101 MHz, CD_2Cl_2, +25°C): δ = –497.7 (s, $\nu_{1/2}$ = 30 Hz, $Ag(P_4)_2^+$ complex); ^{27}Al NMR (78 MHz, CD_2Cl_2, –50°C): δ = 38.1 (s, $\nu_{1/2}$ = 40 Hz, relative low intensity)

Reactions between AsI_3, I_2 and $Ag[Al(OR)_4]$

Reaction 1 (in CH_2Cl_2 solution): $Ag[Al(OR)_4]$ (0.707 g, 0.658 mmol), AsI_3 (0.297 g, 0.658 mmol) and I_2 (0.166 g, 0.658 mmol) were placed in the two bulbed vessel. Cooled (–78°C) CH_2Cl_2 was transferred onto the solid mixture and the flask was kept at –78°C. The flask was occasionally shaken and warmed to about –30°C for a short time. After cooling of the reaction mixture to –78°C, reversible precipitation of voluminous dark solids was observed ($Ag(I_2)_n^+$?, AsI_3 remained insoluble at –78°C). The precipitation of AgI occurred only very slowly when storing the reaction flask at –30°C and the isolated crystals were only the substrates AsI_3 and I_2 (unit cell determinations). At about 0°C the precipitation of AgI occurred with an increased rate and was almost quantitative at ambient temperature. An NMR tube reaction was prepared similarly and it was analyzed after precipitation of silver iodide by ^{13}C, ^{27}Al and ^{19}F NMR. In the ^{13}C NMR signals of at least 3 different $–CF_3$ groups (three quartets) could be observed but none of them could be assigned to the intact $[Al(OR)_4]^-$ anion. Although the concentration of the sample was high enough to usually obtain a good quality ^{27}Al NMR spectrum at a low number of scans, we recorded only a weak sharp signal assigned to the $[Al(OR)_4]^-$ at the limit of detection (with 8192 scans!). ^{19}F NMR spectra were recorded at 223K, 243K and 263K. At the spectra there are 6 signals at 223K up to 14 signals at 263K observed (poor solubility) belonging to the decomposition products. The most intensive signal at δ = –71.9 shows a fine structure at 223K.

^{13}C NMR (63 MHz, CD_2Cl_2, –30°C): δ = 120.2 (q, J_{CF} = 290.7 Hz, CF_3, most intensive signals), 120.4 (q, J_{CF} = 291.0 Hz, CF_3, middle intensive signals), 119.9 (q, J_{CF} = 290.0 Hz, CF_3, the weakest signals); ^{27}Al NMR (78 MHz, CD_2Cl_2, –20°C): δ = 37.1 (s, $\nu_{1/2}$ = 30 Hz), ^{27}Al NMR (78 MHz, CD_2Cl_2, RT): δ = 36.8 (s, $\nu_{1/2}$ = 50 Hz); ^{19}F NMR (235 MHz, CD_2Cl_2, –50°C) δ = –70.5 (s, 1F), –71.9 (s, 5F), –74.1 (s, 1F), –75.6 (s, 1F), –75.7 (s, 1F), –75.9 (s, 1F); ^{19}F NMR (235 MHz, CD_2Cl_2, –30°C) δ = –70.5 (s, 10F), –71.8 (s, 2F), –71.9 (s, 40F), –72.0 (s, 2F), –72.4 (s, 1F), –74.1 (s, 7F), –75.5 (s, 3F), –75.6 (s, 4F), –75.7 (s, 8F), –75.9 (s, 7F); ^{19}F NMR (235 MHz, CD_2Cl_2, –10°C) δ = –69.6 (s, 1F), –70.5 (s, 10F), –71.8 (s, 1F), –71.9 (s, 40F), –72.0 (s, 3F), –72.3 (s, 3F), –72.4 (s, 4F), –74.1 (s, 5F), –75.6 (s, 10F, broad), –75.7 (s, 1F), –75.9 (s, 10F, broad), –76.1 (s, 1F)

Reaction 2 (in the solid state): Ag[Al(OR)$_4$] (0.432 g, 0.402 mmol), AsI_3 (0.184 g, 0.402 mmol) and I_2 (0.102 g, 0.402 mmol) were ground in an achate mortar under an inert atmosphere of Ar. The mixture became homogenous after few minutes, but when left untouched for a while, the iodine crystallized visibly on the rose-pink surface of the mixed solids. The IR sample was prepared in Nujol but the rose-pinky color disappeared immediately after suspending the mixture in oil. The sample got yellow (AgI) due to decomposition. The recorded spectrum was of bad quality but the band at 650 cm^{-1}, assigned to the Al–F vibration of the $[(RO)_3Al–F–Al(OR)_3]^-$ anion, confirmed the decomposition.

Reaction 3, in the NMR tube between AsI_3, I_2, CS_2 and Ag[Al(OR)$_4$]: Ag[Al(OR)$_4$] (0.305 g, 0.263 mmol), AsI_3 (0.120 g, 0.263 mmol) and I_2 (0.067 g, 0.263 mmol) were loaded into the bulb of a Schlenk vessel connected through a frit plate with a NMR tube glass-blown onto it. The mixture of solvents CS_2 and CH_2Cl_2 (1:2) was added at –78°C. The flask was kept at -78°C being occasionally shaken. No AgI was formed at this temperature and most AsI_3 was undissolved. Dark voluminous solids precipitated at –78°C (Judged upon the volume, too much for the I_2 used in this reaction) that could be dissolved again above about –50°C. The flask was stored at –78°C for one day and at –25°C for another. During this time only very small amounts of yellow solids precipitated (AgI?). The solvent was evaporated and changed for CD_2Cl_2. The NMR tube was closed and warmed to about 0°C. Yellow AgI was formed immediately and the tube was cooled again to –78°C. The ^{13}C NMR spectrum shows four sets of quartets indicating a decomposition of the anion (about 70% anion is decomposed). However, the ^{27}Al NMR shows only signal of not decomposed anion at δ = 37.1, probably because all the Al containing decomposition products gave very broad signals and were therefore not noticed.

^{13}C NMR (63 MHz, CD_2Cl_2, –30°C): $\delta = 120.9$ (q, $J_{CF} = 292.3$ Hz, CF_3, not decomposed anion, most intensive signal), 120.4 (q, $J_{CF} = 291.6$ Hz, CF_3), 120.2 (q, $J_{CF} = 290.7$ Hz, CF_3), 119.9 (q, $J_{CF} = 290.4$ Hz, CF_3, signals of the lowest intensity); ^{27}Al NMR (78 MHz, CD_2Cl_2, +25°C): $\delta = 37.1$ (s, $\nu_{1/2} = 25$ Hz, relative low intensity).

Reaction between I_2 and $Ag[Al(OR)_4]$

$(CH_2Cl_2)Ag[Al(OR)_4]^-$ (0.395 g, 0.340 mmol) and I_2 (0.087 g, 0.340 mmol) were placed in a two bulbed vessel followed by CS_2 (1 ml) and CH_2Cl_2 (4 ml). When the reaction mixture was kept below –20°C, the solution had a dark violet color. After warming the flask to ambient temperature a yellow voluminous solid precipitated and the solution over it turned cherry red. The solution was than filtered from the precipitate and tested on Ag^+ (negative) and I_2/I^- (positive). Than all volatiles were removed in vacuuo and from the residue a sample for NMR and mass spectrometry was taken.

^{13}C NMR (63 MHz, CD_2Cl_2, RT): no signal of $C(CF_3)_3$ was observed, no detectable amounts of the anion or any of its decomposition product were present in the NMR tube. ^{27}Al NMR (78 MHz, CD_2Cl_2, RT): $\delta = 53.0$ (s, $\nu_{1/2} = 4692$ Hz, low intensity, a large number of scans required). Mass spectrometry: only low molecular weight peaks were recorded up to M/z = 368.4 , most intensive at M/z = 69 (CF_3^+). The $M(I_2^{\bullet+}) = 253.8$ was also detected.

Other Deposited Sections

Tab. A. Fluorine contacts of the $AsBr_4^+$ cation in the $AsBr_4^+[Al(OR)_4]^-$

As–Br···F contacts	Length of contact	As–Br···F contacts	Length of contact
Br4···F4	3.265	Br2···F35	3.537
Br4···F17	3.237	Br2···F20	3.254
Br4···F1	3.538	Br2···F1	3.481
Br4···F2	3.597	Br1···F21	3.454
Br3···F31	3.360	Br1···F35	3.482
Br3···F5	3.098	Br1···F12	3.409
Br3···F7	3.443	Br1···F16	3.223
Br3···F1	3.504	Br1···F33	3.454
Br3···F36	3.527		

Tab. B Total energy, zero point energy, solvation energy and thermal and entropic contributions at 298K to the free energy of the $Ag(CH_2Cl_2)_3^+$ (C_2), AsI_3 (C_{3v}), $Ag(AsI_3)_2^+$ (C_2) and CH_2Cl_2 (C_{2v}) species (at MP2/TZVPP level).

Molecule (symmetry)	*U (MP2/TZVPP)*	*ZPE (MP2/TZVPP)*	*H_{solv}(BP86/SVP) COSMO*	*Thermal+Entropic correc. to G at 298K*
$Ag(CH_2Cl_2)_3^+$ (C_2)	–3022.16690	0.08808	–0.06004	0.03902
AsI_3 (C_{3v})	–2268.50920	0.00223	–0.00407	–0.02659
CH_2Cl_2 (C_{2v})	–958.61384	0.02794	–0.00404	0.00621

Tab. C. Total energy, zero point energy, solvatation energy and thermal and entropic contributions at 298K to the free energy of all calculated species in [H] (at MP2/TZVPP level).

Molecule (symmetry)	*U (MP2/TZVPP)*	*ZPE (MP2/TZVPP)*	*H_{solv}(BP86/SVP) COSMO*	*Thermal+Entropic correc. to G at 298K*
$AsBr_2^+$ (C_{2v})	–7379.34087	0.00197	–0.08149	–0.02874
AsI_2^+ (C_{2v})	–2256.84173	0.00158	–0.07563	–0.03070
PBr_2^+ (C_{2v})	–5485.74848	0.00264	–0.07953	–0.02701
PI_2^+ (C_{2v})	–363.24680	0.00221	–0.07384	–0.02902
$AsBr_4^+$ (T_d)	–12524.56758	0.00444	–0.06447	–0.03171
AsI_4^+ (T_d)	–2279.56412	0.00335	–0.06262	–0.03606
PBr_4^+ (T_d)	–10630.99836	0.00574	–0.06472	–0.02926
PI_4^+ (T_d)	–385.98251	0.00444	–0.06119	–0.03382
$As_2Br_5^+$ (C_s)	–17331.67684	0.00608	–0.06210	–0.04104
$As_2I_5^+$ (C_s)	–4525.41879	0.00490	–0.05905	–0.04589
$P_2Br_5^+$ (C_s)	–13544.51217	0.00830	–0.06013	–0.03617
$P_2I_5^+$ (C_s)	–738.24532	0.00686	–0.05709	–0.04130
$AsBr_3$ (C_{3v})	–9952.28126	0.00283	–0.00353	–0.03156
AsI_3 (C_{3v})	–2268.50920	0.00223	–0.00407	–0.03460
PBr_3 (C_{3v})	–8058.68874	0.00368	–0.00188	–0.02972
PI_3 (C_{3v})	–374.91413	0.00301	–0.00281	–0.03386
Br_2 ($D_{\infty h}$)	–5145.14283	0.00076	–0.00165	–0.02236
I_2 ($D_{\infty h}$)	–22.65132	0.00054	–0.00256	–0.02593
AgBr ($C_{\infty v}$)	–2719.12161	0.00056	–0.01338	–0.02495
AgI ($C_{\infty v}$)	–157.86742	0.00047	–0.01270	–0.02580
$Ag(CH_2Cl_2)_3^+$ (C_2)	–3022.16690	0.08808	–0.06004	0.02628
$AsI_2PI_3^+$ (C_s)	–2631.83662	0.00599	–0.05937	–0.04339
$PI_2AsI_3^+$ (C_s)	–2631.82631	0.00575	–0.05836	–0.04382

Tab. D. Total energy, zero point energy, solvation energy and thermal and entropic contributions at 298K to the free energy of the species calculated at BP86/SV(P) level.

Molecule (symmetry)	*U (BP86/SVP)*	*ZPE (BP86/SVP)*	*H_{solv}(BP86/SVP) COSMO*	*Thermal+Entropic correction to G at 298K*
$AsBr_2OR$ (C_1)	–8509.68048	0.05578	–0.00345	–0.00232
AsI_2OR (C_1)	–3384.32644	0.05524	–0.00394	–0.00460
PBr_2OR (C_1)	–6615.06049	0.05696	–0.00203	0.00011
PI_2OR (C_1)	–1489.70224	0.05632	–0.00295	–0.00219
$AsBr_2^+$ (C_{2v})	–7383.89792	0.00177	–0.08175	–0.02916
AsI_2^+ (C_{2v})	–2258.55901	0.00139	–0.07543	–0.03116
PBr_2^+ (C_{2v})	–5489.26679	0.00236	–0.08169	–0.02747
PI_2^+ (C_{2v})	–363.92351	0.00189	–0.07558	–0.02960
$Al(OR)_4^-$ (S_4)	–4744.54880	0.21804	–0.04035	0.09155
$Al(OR)_3^-$ (D_{3h})	–3618.91753	0.16453	–0.00272	0.06591

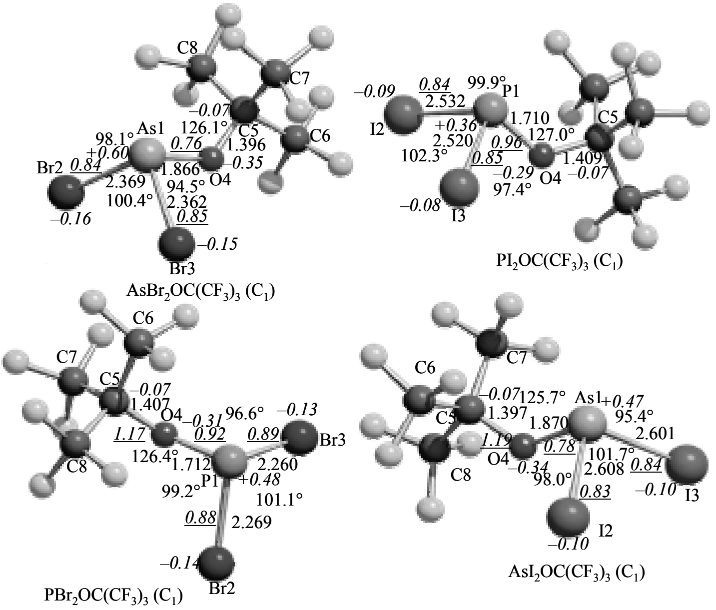
$AsBr_2OC(CF_3)_3$ (C_1)
$PI_2OC(CF_3)_3$ (C_1)
$PBr_2OC(CF_3)_3$ (C_1)
$AsI_2OC(CF_3)_3$ (C_1)

Fig. A. The EX_2OR species - the products of decomposition of the $EX_2^+[Al(OR)_4]^-$ salts in the Ligand Abstraction Reaction (Eq. 14): $AsBr_2OR$ (C1), AsI_2OR (C_1), PBr_2OR (C_1) and PI_2OR (C_1) (R = $C(CF_3)_3$). Calculated partial charges (“Paboon”) are given in italics, shared electron numbers (SEN) are given in italics and are underlined. All species are true minima with no imaginary frequencies.

Decomposition of the anion

Since ^{75}As NMR spectrometry in most cases (except for **1**) was useless in the detection of decomposition products or intermediates, information about the decomposition of the anion gave the ^{13}C NMR (we cannot obtain routine ^{19}F NMR in our department). To assign anion decomposition without doubt, we recorded the ^{13}C NMR spectra of a freshly prepared CD_2Cl_2 solution of $Ag[Al(OR)_4]$; $R = C(CF_3)_3$) at temperatures between 193K and 300K (Tab. E, deposited section). The ^{13}C NMR signals of the CF_3 groups (quartet) in the $[Al(OR)_4]^-$ anion shift from $\delta = 121.4$ at r.t. to $\delta = 120.3$ (193K). Usually the (partial) decomposition of the anion led to an additional quartet in the ^{13}C NMR (of lower intensity) shifted by about -0.5 to -0.6 ppm. It is likely, that the $[(RO)_3Al–F–Al(OR)_3]^-$ anion is one major decomposition product, since its reported ^{13}C NMR shifts agree with our observation. In the reaction of PCl_3 with $Ag[Al(OR)_3]$ we found direct proof for the quantitative formation of $[(RO)_3Al–F–Al(OR)_3]^-$.[37]

Tab. E. Temperature dependence of the ^{13}C NMR shift of the quartet of $–CF_3$ groups of the anion $[Al(OR)_4]^-$ ($R = C(CF_3)_3$) in CD_2Cl_2. The measurement was carried out on the sample of freshly prepared $Ag[Al(OR)_4]$ in intervals of 10°K from 193K to 283K and at 300K (RT).

Temperature [K]	**$–CF_3$ shift [ppm]**	**CD_2Cl_2 [ppm]**
193	120.34	53.73
203	120.50	53.73
213	120.60	53.72
223	120.71	53.73
233	120.81	53.73
243	120.91	53.73
253	121.02	53.73
263	121.15	53.73
273	121.29	53.73
283	121.40	53.73
300 (RT)	121.42 (121.52)	53.63 (53.73)

Assignment of the IR spectrum of two fractions of $I_2As–PI_3^+$

For clarity, the spectra in Fig. B are shown in the range between 200 cm^{-1} and 500 cm^{-1}. There are no unassigned vibrations in the entire measured range of 200-4000 cm^{-1} (See Table F).

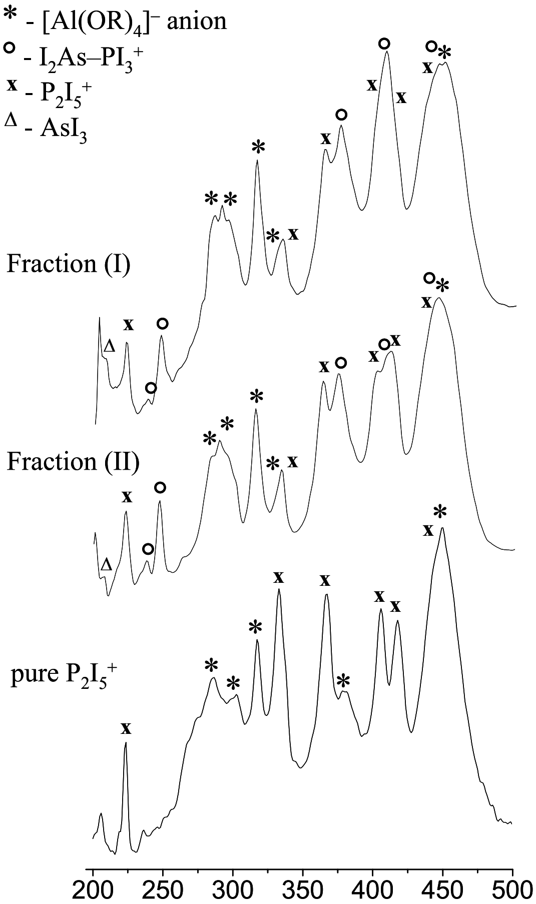

Fig. B. The IR spectra of the mixture of two products in reaction (10): $I_2As–PI_3^+$ and $P_2I_5^+$ (fraction I and II) and the spectrum of pure $P_2I_5^+[Al(OR)_4]^-$. The spectra are only shown between 200 cm^{-1} and 500 cm^{-1}, where $P_2I_5^+$ and $I_2As–PI_3^+$ vibrations occur.

We compared the spectra of fraction I and II with the spectrum of the crystalline $P_2I_5^+$ salt (at the bottom of Fig. B). The vibrations assigned to $P_2I_5^+$ at 413, 401, 364, 330 and 223 cm^{-1} are also found in spectrum of fraction II and fraction I (in spectrum I the bands at 402 cm^{-1} and 412 cm^{-1} became shoulders of the intense vibration at 408 cm^{-1}). The 430 cm^{-1} band in the $P_2I_5^+$ spectrum was assigned as a shoulder of the anion band (at 445 cm^{-1}). In the spectra II and I those vibrations cannot be distinguished. Other bands (except that at 206 belonging to AsI_3) were clearly assigned to the cation **2**: 408, 375, 247 and 237 cm^{-1} and are not present in the $P_2I_5^+$ spectrum (see Tab. F and 2). The more crystalline fraction I contains more of cation

2 than the fraction II. Thus, we observe that in spectrum I an absorption at 408 cm^{-1} is more intense than in spectrum II, so that the 402 cm^{-1} and 412 cm^{-1} bands are recognizable in fraction II but not in fraction I. The vibration of **2** at 375 cm^{-1} is relatively stronger than in the spectrum of fraction II. The bands at 375, 247 and 237 cm^{-1} are not present in the $P_2I_5^+$ spectrum and therefore belong to **2** (see Fig. 10). The frequency calculation performed at the MP2/TZVPP level for **2** is in good agreement with these assignments (results included in Tab. F and 2).

Tab. F. Experimental and calculated vibrations of $I_2P–PI_3^+$ and $I_2As–PI_3^+$.

$I_2AsPI_3^+$ + $P_2I_5^+$ fr. I/II	$I_2As–PI_3$ in I/II	$P_2I_5^+$ in I/II	Pure $P_2I_5^+$	$I_2As–PI_3^+$ calc. (IR: %)	$P_2I_5^+$ calc (IR: %)	Anion in fr I/II	Anion in **1**	Anion in $CS_2Br_3^+$ $[Al(OR)_4]^-$	Anion Calc.
440 a)	440 a)	440 a)	430(sh)	443(vs)	462(s)	1350(s)	1352(m)	1353(ms)	1344(s)
412(s)	-	412(s)	413(s)	-	437(vs)	1305(s)	1298(s)	1301(s)	-
408(vs)	408(vs)		-	433(vs)	-	1275(vs)	1274(vs)	1276(vs)	1260(vs)
402(s)	-	402(s)	401(s)	-	420(s)	1258(vs)	1244(vs)	1242(vs)	1230(vs)
375(s)	375(s)	-	-	394(m)	-	1248(vs)	1222(vs)	1219(vs)	1216(vs)
364(s)	-	364(s)	364(s)	-	389(s)	1216(vs)	1164(s)	1169(ms)	1196(w)
334(m)		334(m)	330(s)	-	354(w)	1161(s)	1134(sh)	1133(sh)	1136(w)
247(m)	247(m)	-	-	268(m)	-	1136(s)	1074(sh)	1075(sh)	1110(w)
237(w)	237(w)	-	-	254(w)	-	975(vs)	973(vs)	973(vs)	960(s)
223(m)	-	223(m)	223(m)	-	235(w)	864(m)	833(m)	832(m)	816+826(w)
206(w) b)	-	-		-	-	831(m)	756(w)	755(w)	736(w)
				185(w)	142(vw)	755(w)	727(s)	728(s)	710(m)
				127(vw)	107(0)	728(s)	572(w)	571(w)	556(w)
				100(0)	105(vw)	636(m)	561(w)	561(mw)	546(mw)
				92(vw)	88(0)	579(m)	536(m)	537(mw)	520(w)
				84 (0)		560(m)	445(m)	445(m)	420+437(mw)
				69 (0)		537(s)	380(vw)	365-427(sh)	352+365(w)
				63 (0)		446(s)	367(vw)	330(vw)	319(w)
				50 (0)		330(sh)	330(vw)	314(w)	301(w)
				42 (0)		315(m)	315(w)	284(w)	274(w)
				25 (0)		290(m)	281(vw)		

a) a vibration of $I_2As–PI_3^+$ (calc. 443 cm^{-1}) overlapped with $P_2I_5^+$ and anion vibration (at 445 cm^{-1}), therefore not seen, b) vibration of AsI_3 (found in the Raman spectrum of pure AsI_3 at 207 cm^{-1}).

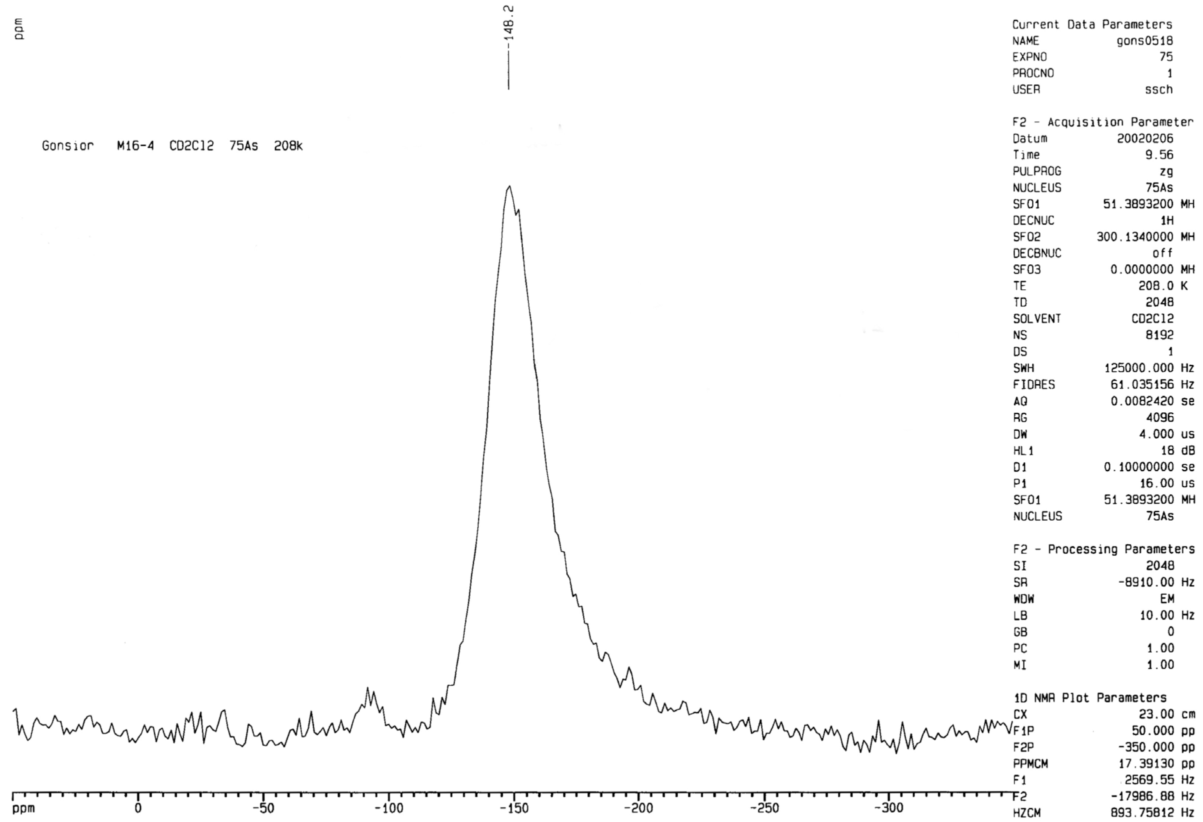

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Fig. C. ^{75}As NMR spectrum of $AsBr_4{}^+[Al(OR)_4]^-$ recorded on the in situ NMR tube reaction at – 70°C. The signal of $AsBr_4{}^+$ cation appeared at – 148.2 ppm.

$$\begin{tikzcd}
EX_{3(g)} & +\,Ag(CH_2Cl_2)_3{}^+_{(g)} \arrow[r, "\Delta_rG_{(g)}"] & EX_2{}^+_{(g)} \arrow[d, "-\Delta G_{(solv)}(\mathbf{C})"'] & +\,AgX_{(g)} \arrow[d, "-\Delta H_{(subl)}(\mathbf{D})"'] & +\,3CH_2Cl_{2(g)} \arrow[d, "-\Delta H_{(vap)}(\mathbf{E})"'] \\
EX_{3(s)} \arrow[u, "+\Delta H_{(subl)}(\mathbf{A})"] & +\,Ag(CH_2Cl_2)_3{}^+_{(solv)} \arrow[u, "+\Delta G_{(solv)}(\mathbf{B})"] \arrow[r, "\Delta_rG_{(CH2Cl2)}"] & EX_2{}^+_{(solv)} & +\,AgX_{(s)} & +\,3CH_2Cl_{2(l)}
\end{tikzcd}$$

Fig. D. The Born-Haber cycle for the formation of the $EX_2{}^+$ cation in CH_2Cl_2 solution for E = As, P and X = Br, I

Tab. G. The entries in the Born-Haber cycle in Fig. D (in kJ·mol^{-1}) of the reaction EX_3 + $Ag(CH_2Cl_2)_3^+ \rightarrow EX_2^+ + AgX + 3CH_2Cl_2$ (*X = Br, I; E = As, P*). For the definition of the A-D see Fig. D.

E, X	**A**	**B**	**C**	**D**	**E**	**$\Delta_rG_{(g)}$**	**$\Delta G^{298K}_{(CH_2Cl_2)}$**	**No AgX↓**
As, Br	+41,8	+158,0	–214,0	–217,4	–87,0	+244,0	–75	108
As, I	+59,3	+158,0	–198,6	–196,9	–87,0	+196,0	–69	95
P, Br	+38,8	+158,0	–208,8	–217,4	–87,0	+243,0	–73	109
P, I	+43,9	+158,0	–193,9	–196,9	–87,0	+198,0	–78	86